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THE OPTICS OF MIRAGES

By C. V. Raman and S. Pancharatnam

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1. Introduction

Chapter IV of the celebrated *Traite de la Lumiere* by Christiaan Huyghens published in the year 1690 deals with "the Refraction of the Air". Huyghens discussed the effects which arise by reason of the atmosphere having a refractive index varying with the height above the surface of the earth and also with the physical conditions. The problem was considered by him from two distinct points of view, *viz.*, that light consists of rays travelling out from the source, alternatively of wave-fronts propagated through the medium; he showed that the two approaches give completely identical results. Each small piece of the wave-front in an inhomogeneous but isotropic medium moves forward normally to itself with the velocity appropriate to the refractive index at its position; the pieces thus moving forwards join up to form a continuous wave-front. As the result, we find that the rays of light traverse curved paths which are everywhere normal to the wave-fronts.

Mirages constitute one of the most remarkable effects arising from a variation of refractive index of the atmosphere. A very familiar type of mirage is that seen when the light rays are nearly parallel to the heated surface of the earth; the sky and objects on the horizon then appear to be reflected by the surface or rather by the cushion of hot air in contact with it. The phenomenon is frequently observed over asphalted or concrete roads on sunny days and over firm smooth sands in warm weather. Very striking pictures of such mirages are reproduced in a book by Minnaert.[1] Mirages can also be artificially reproduced in the laboratory. R. W. Wood[2] in his *Physical Optics* gives photographs of the phenomenon as thus obtained.

On an examination of the explanations usually given for the formation of mirages, it becomes apparent that they are inadequate and indeed unsatisfactory. The authors felt that the subject should be investigated more fully both from the theoretical and the experimental standpoints. The present memoir records the results of such study and throws new light on the nature and origin of mirages.

2. THE NATURE OF THE PROBLEM

Consider two media of refractive indices μ_1 and μ_2 which we suppose in the first instance to have a sharp plane boundary of separation that is normal to the z-direction. If a plane wave from the first medium be incident on the boundary at a glancing angle ϕ_1 then, in general, there would exist both a reflected and a refracted wave; the former follows the usual law of reflection, while the direction ϕ_2 of the latter is given by Snell's law of refraction $\mu_1 \cos\phi_1 = \mu_2 \cos\phi_2$, the intensities of the reflected and refracted beams being given by Fresnel's formulæ. If however $\mu_1 \cos\phi_1 > \mu_2$, there exists no refracted beam, so that the incident energy is totally reflected.

In the present paper, we are interested in the case in which the change from the refractive index μ_1 to the refractive index μ_2 does not occur abruptly at a sharp boundary, but takes place continuously and progressively over a certain transition layer—the refractive index being constant along planes normal to the z-direction. In this case, general considerations based on wave-optics show that the refracted wave in the second medium should still satisfy Snell's law of refraction $\mu_1 \cos\phi_1 = \mu_2 \cos\phi_2$ while, if the refractive index does not change appreciably within distances of the order of the wavelength, there would normally be no reflected wave in the first medium, the entire energy going into the refracted wave. However, an exception to to this statement must clearly arise when $\mu_1 \cos\phi_1 > \mu_2$. Since in these circumstances, there can be no refracted wave in the second medium, a reflected wave must be formed, the reflection being in fact total. Such a situation occurs in the phenomenon of the mirage. Though it is clear that the reflected wave in the first medium must be a plane wave following the usual laws of reflection, the nature of the disturbance within the transiton layer can only be ascertained by a rigorous analytical treatment from wave-theoretical considerations. This has been done by Epstein[3] choosing a particular profile for the refractive index variation and the solution obtained is expressed in terms of hypergeometric functions; however, the only application of Epstein's work which he has made and is relevant to the present problem is to remark that there is total reflection in the conditions mentioned, the angle of incidence being equal to the angle of reflection.

3. SOME ELEMENTARY CONSIDERATIONS

The theory of the mirage which is usually accepted purports to base itself on geometrical optics. Any incident ray initially making an angle ϕ_1 with the plane of the stratifications would be progressively deviated from its course so that when it reaches a limiting layer of refractive index

$\mu_l = \mu_1 \cos \phi_1$, it would be tangential to that layer. It is then usually stated that the ray continues to curve round, but it must be noted that on the basis of geometrical optics the ray should really continue parallel to the stratifications along the limiting layer. This would happen to every one of the rays in the incident beam. As a consequence, the entire energy of the incident radiation would be concentrated in an infinitely thin layer having the refractive index μ_l. If we take two adjacent rays a finite distance apart, the part of the wave-front between them would on entry into the transition layer swing round and at the same time contract in its extension and ultimately become reduced to a point travelling along the limiting layer of refractive index μ_l.

It is evident that the foregoing situation deduced from elementary considerations presents some fundamental difficulties. In the first place, as we have already noted, considerations of a general nature indicate that the energy reaching the limiting layer which cannot penetrate further must of necessity be returned back through the transitional region into the first medium as a reflected wave. Then, again, as has been stressed by Planck[4] in his *Theory of Light*, the equivalence of the results of geometrical optics with the exact results of wave theory is subject to certain limitations. One of them is that the amplitude of the wave-function must be only slowly variable in space. This condition is clearly violated in the present case, for according to what has been said above, the disturbance would be infinitely great at the limiting layer of refractive index μ_l and zero immediately below it. It follows that while the actual facts may bear some resemblance in their general features to this elementary picture, the real situation would nevertheless be rather different; firstly, a reflected wave must emerge from the limiting layer; secondly, there should exist a finite intensity below the limiting layer, while above that layer, the intensity though large would exhibit successive maxima and minima arising from the interference of the incident and reflected waves and progressively diminish as we move from the limiting layer toward the first medium.

It is clear from the foregoing remarks that the situation in the vicinity of the limiting layer would resemble that well-known in physical optics to appear in the vicinity of caustic surfaces formed by reflection or refraction of light. The effects observed in such cases are usually described as due to the propagation of a cusped wave-front along the caustic surface. Such a result is clearly capable of experimental test in the present case and has been confirmed by the observations made by us presently to be described.

4. OBSERVATION OF THE CAUSTIC AND ACCOMPANYING INTERFERENCES

The arrangement first tried for producing the mirage under laboratory conditions was similar to that described by R. W. Wood. A long steel plate, approximately 1½ metres long, 10 cm. in width and 2 cm. in thickness was supported horizontally and heated from below by four gas burners, the upper surface being covered with soot. The arrangement did not prove very satisfactory since the rising of the hot air from the heated surface prevented a sufficiently sharp temperature gradient from being established, while at the same time such phenomena as could be observed were of an exceedingly labile nature owing to the turbulent convection of air near the hot surface. However, the conditions were greatly improved when an electric fan was used to blow away the hot air from above the surface. When this was done, it was possible to see clearly the reflected image of the 'mountain peaks' formed by holding the serrated edge of a cardboard against an illumined ground glass screen at the far end of the plate. The action of the fan in sharpening the temperature gradient was picturesquely revealed by suitably lowering the eye, when a luminous thin cushion of air was seen to form over the heated surface. In order to study the phenomena critically, the object viewed was replaced by an illuminated slit kept parallel to the heated surface and the light diverging from it was rendered parallel by a collimating lens and allowed to fall obliquely on the hot plate. The beam was allowed to cover the whole length of the plate, the angle of incidence being adjusted merely by moving the slit. Further, the plate was heated electrically to ensure a fairly uniform temperature. When the temperature was sufficiently high and the glancing angle sufficiently small, the field at the nearer end of the plate, when examined through a pocket lens, displayed a bright strip of light separated by a dark region from the plane of the hot surface. It was clear, however, that the use of the fan was causing a smearing out of the caustic and preventing phenomena of the nature of interferences from being clearly seen.

The above difficulty was removed by the artifice of turning the plate edgewise so that the hot surface was now vertical, though its length remained horizontal. The hot air now flowed up in streamlines parallel to the surface of the plate, thus rendering the use of the fan unnecessary. With the slit now vertical, it was possible to observe clearly with the aid of a pocket lens a bright caustic bordered by a large number of interferences of the type referred to in the last section. A photograph of this phenomenon is given in Plate XII, Fig. 1. In order to completely arrest the oscillations of the caustic and its fringes, a short exposure (1/100th of a second) was necessary so that the slit had to be brilliantly illuminated. Accordingly, sunlight was

used for this purpose and this, in fact, enabled also the introduction of a red filter for increasing the clarity of the fringes.

It will be seen that the field in Plate XII, Fig. 1 consists of three parts. To the right of the bright caustic (*i.e.*, towards the heated surface) the field is dark, while to its left lies an illumined strip containing a large number of interference fringes whose separation narrows down to a constant value as we move away from the caustic; this is of course due to the increasing inclination between the two branches of the cusped wave-front. Since the heated plate is necessarily of finite extension, the reflected part of the cusped wave-front does not extend to infinity but is terminated. This manifests itself in the field of view by the occurrence of a second edge to the left of which the intensity is considerably less (though not zero), the edge being bordered by some broad fringes.

5. Relation of the Mirage to the Cusped Wave-Front

The actual mirage is observed when the eye is kept at any point which lies on the bright strip of light lying to the left of the caustic, the eye being focussed on the plane containing the object, *i.e.*, at infinity. It is to be expected that two images would then be seen whose positions lie respectively along the directions of the normals drawn from the eye to the two branches of the cusped wave-front leaving the nearer edge of the plate. In fact, the fringes observed to the left of the caustic in Plate XII, Fig. 1 may be regarded as due to the interference between the light from two such virtual sources, the progressive narrowing of the spacing of the fringes to the left of the caustic corresponding to the increasing separation of the sources. That the separation of the two images observed depends on the position of the eye or aperture through which the phenomenon is viewed is illustrated in Plate XII, Fig. 3. In order to make the nature of the image evident, the serrated edge of a hacksaw blade has been used to form one of the edges of the slit. An aperture was kept in front of the lens and the succession of photographs exhibit the alteration in the phenomena as the aperture is gradually moved to the left. When the aperture is on the bright caustic, a single image is seen, while as it is moved to the left this separates into two images, one of which is a direct (or more properly, a refracted) image, the second being an inverted reflected image, the separation between the two gradually increasing. A remarkable feature of the sequence of phenomena illustrated in Plate XII, Fig. 3 is the occurrence of a third erect image close to the reflected image in the fourth and fifth photographs of the sequence; this image starts developing when the aperture has been moved towards the outer edge of the central illumined strip (where broad fringes start appearing

in Plate XII, Fig. 1), becoming coincident with the reflected image when the aperture is exactly at the edge mentioned. As the aperture is moved further left, only the 'direct' image continues to be visible, as is shown in the last photograph of the sequence; this is to be expected since the reflected part of the cusped wave-front is no longer received through the aperture.

The third image mentioned above can be cut off by inserting an opaque screen near the farther end of the heated plate and adjusting it so that its edge protrudes a little beyond the surface of the plate. This shows that the image is due to the ordinary refraction of rays directly entering the edge of the heated layer at the farther end of the plate. The main features of the path of such rays may be deduced from the experimental observations described in the previous paragraph. The terminus of the reflected part of the cusped wave-front corresponds to certain limiting rays entering the region at the farther end of the plate. Rays which are able to enter the edge of the heated layer at a closer distance to the plate than these limiting rays proceed a longer distance before emerging from the heated stratum and also suffer a larger deviation. These rays give rise to the erect third image; in fact, the second refracted wave-front, obtained by drawing the surfaces orthogonal to these rays, meets the termination of the reflected part of the wave-front so as to form a second cusp.

It may be mentioned that an erect third image has been observed and photographed by Hiller[5] in his study of the mirage produced by a long vertical wall. He has attributed the phenomenon to multiple reflection, but it is more probably due to ordinary refraction as in the present case.

Till now we have dealt mainly with the case when the distant object is of negligible angular dimensions. When an object of finite angular dimensions is used, the point on the image which corresponds to any particular point on the object is to be determined as before for each setting of the eye. In this case there will be a distortion of the images because the position of the limiting layer as well as the inclinations of the cusped wave-fronts corresponding to any particular point on the object varies with the position of the object-point. Plate XII, Fig. 2 shows the photographs taken using as the object a small model of a bird made of glass. This was placed near the focal point of the collimating lens. The sequence of photographs show the variation in the appearance of the phenomena as the eye is moved away from the plate. The appearance of a third erect image in addition to the usual reflected image may be discerned in the last two photographs of the sequence.

6. Mathematical Treatment

Let the z-axis be taken normal to the direction of the stratifications of refractive index, the plane of incidence being taken as the xz plane. The disturbance ψe^{iwt} at every point must satifsy the wave equation

$$\nabla^2\psi + k^2\mu^2\psi = 0$$

Since the refractive index is a function only of z, we may put $\psi = e^{ikpx}u\,(z)$ where u satisfies the one-dimensional wave equation

$$\frac{d^2u}{dz^2} + \mathrm{Q}^2\,(z)\,u = 0 \tag{1}$$

where

$$\mathrm{Q}\,(z) = k\sqrt{\mu^2 - p^2} \tag{2}$$

We shall take the layer at which the refractive index becomes equal to p to be the plane $z = 0$, and the law of variation of refractive index to be given by

$$\left.\begin{aligned} \mu^2 &= \mu_1^2 \qquad \text{for} \quad z \geq z_1 \\ \mu^2 &= \alpha^2 z + p^2 \qquad \text{for} \quad z \leq z_1 \end{aligned}\right\} \tag{3}$$

The general solution of the wave equation (1) for the region $z \geq z_1$, can be written

$$\begin{aligned} u = \mathrm{A}\,\{&\exp. - ik\,(\sqrt{\mu_1^2 - p^2}z + \theta) \\ &+ \mathrm{R}\exp. ik\,(\sqrt{\mu_1^2 - p^2}z + \theta)\} \end{aligned} \tag{4}$$

If the incident wave be given by $\mathrm{A}\exp. - ik\,(\mu_1 \sin\phi_1 \cdot z + \theta)$, the first term will represent the incident wave with $p = \mu_1 \cos\phi_1$ so that from (3) the plane $z = 0$ is the limiting layer; the second term represents a reflected wave with the angle of reflection equal to the angle of incidence, R being the coefficient of reflection. We shall take R to be a real quantity, since this can be ensured by appropriately choosing the phase factor θ, the complex reflection coefficient being $\mathrm{R}e^{2i\theta}$.

Writing $k\alpha = 3\gamma/2$ the wave equation for the region $z \leq z_1$ can be written

$$\frac{d^2u}{dz^2} + \left(\frac{3}{2}\gamma\right)^2 zu = 0 \tag{5}$$

This is one of the transformations of Bessel's equation, the general solution being expressed in terms of the cylinder functions of order one-third:

$$u = z^{1/2}\,C_{1/3}\,(\gamma z^{3/2})$$

i.e., with the usual notation for the Bessel functions

$$u = \xi^{1/3} \{A_1 J_{1/3}(\xi) + B_1 J_{-1/3}(\xi)\} \tag{6}$$

where $\xi = \gamma z^{3/2}$.

For negative values of z the above may be rewritten to avoid the use of imaginary arguments, by putting

$$\xi = i \mid \xi \mid = i\gamma \mid z \mid^{3/2}$$

$$u = \xi^{1/3} \{A_1 I_{-1/3}(\mid \xi \mid) - B_1 I_{1/3}(\mid \xi \mid)\}$$

$$= \xi^{1/3} \left\{A_1 \frac{2}{\pi} \sin \frac{\pi}{3} K_{1/3}(\mid \xi \mid) + (A_1 - B_1) I_{1/3}(\mid \xi \mid)\right\}$$

Since $I_{1/3}(\mid \xi \mid)$ tends to infinity as $z \rightarrow -\infty$, the condition that u remain finite below the limiting layer gives $A_1 = B_1$. Hence below the limiting layer $z = 0$, we have

$$u = \frac{\sqrt{3}}{\pi} \mid \xi \mid^{1/3} A_1 K_{1/3}(\mid \xi \mid) \tag{7}$$

while above the limiting layer

$$u = A_1 \xi^{1/3} \{J_{1/3}(\xi) + J_{-1/3}(\xi)\} \tag{8}$$

For layers not close to the limiting layer, the asymptotic expansion of (8) for large z may be used:

$$u \sim \left(\frac{3}{2\pi}\right)^{1/2} \xi^{-1/6} A_1 \cdot 2 \cos\left(\xi - \frac{\pi}{4}\right)$$

$$\sim \left(\frac{3}{2\pi}\right)^{1/2} \xi^{-1/6} A_1 \left\{\text{exp.} - i\left(\xi - \frac{\pi}{4}\right) + \text{exp.}\, i\left(\xi - \frac{\pi}{4}\right)\right\} \tag{9}$$

The constants A_1 and θ may be determined by the condition that the solutions (4) and (8) must join smoothly, *i.e.*, by the condition that u and du/dz must be continuous at $z = z_1$. Since the solution u as given by (8) is a real quantity below the plane z_1, it is clear from (4) that the reflection coefficient R must be unity, as is to be expected. The constants A_1 and θ may be determined with sufficient accuracy by equating separately the amplitudes and arguments of the periodic functions in (4) and (9) since it is the periodic functions which contribute mainly to du/dz.

Thus

$$A_1 \sim \left(\frac{2\pi}{3}\right)^{1/2} \xi_1^{1/6} A$$

$$\theta \sim \left(\xi_1 - \frac{\pi}{4}\right) - \mu_1 \sin \phi_1 z_1 \tag{10}$$

where $\xi_1 = \gamma z_1^{3/2}$.

Before proceeding to discuss the solution obtained, we may remark that the function ξ in terms of which the solution is expressed can be given a physical interpretation. Using the fact that $\xi = \int_0^z Q dz$, it may be easily verified that

$$[\xi(z) + kpy] = \int_0^P \mu ds$$

where the right-hand side represents the optical distance from the point $P(x, z)$ to the limiting layer, measured along the limiting ray of geometrical optics. Thus in (9) the solution has been represented as the sum of two disturbances, the surface of constant phase of one of the wave-fronts being taken to be that given by geometrical optics; the other reflected wave-front is symmetrical to the first but has suffered a phase change of $\frac{1}{2}\pi$. The asymptotic solution (9) does not apply near the limiting layer as may also be seen by the fact that it gives an infinite intensity at that layer. The correct solution (8) applicable near the limiting layer may be written in a form similar to (9)

$$u = A_1 \xi^{1/3} \frac{J_{1/3}(\xi) + J_{-1/3}(\xi)}{2 \cos(\xi - \frac{1}{4}\pi)} \{\text{exp.} - i(\xi - \tfrac{1}{4}\pi) + \text{exp. } i(\xi - \tfrac{1}{4}\pi)\} \tag{11}$$

Thus, the foregoing mathematical treatment provides a justification for the qualitative description given earlier in the paper of the optical field as a cusped wave which moves along the limiting layer.

Using equations (7) and (8) and a table of Bessel functions, the function $(u/A_1)^2$ which is proportional to the intensity has been plotted against $|\xi|^{2/3}$ which is proportional to the distance z from the limiting layer. The graph is shown in Fig. 1 in the text. It is seen that slightly above the limiting layer there is a large concentration of intensity. Above this again we have a series of interferences which progressively diminish in spacing and intensity, while below the maximum, the intensity rapidly falls to zero.

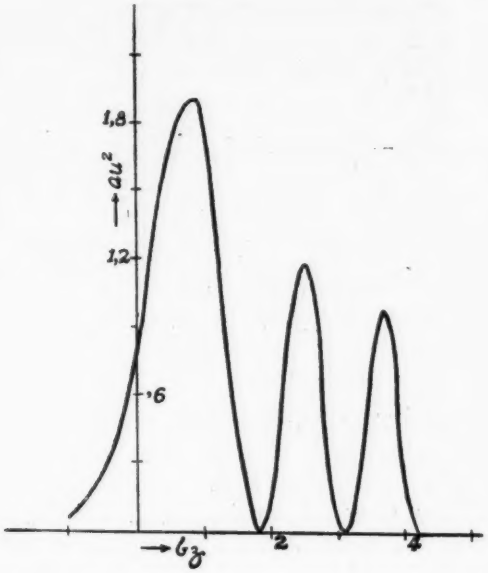

FIG. 1

It will be seen that the method of solution adopted is similar to that adopted in quantum mechanics where similar mathematical problems arise. In fact, though we have for simplicity considered only the case when μ^2 varies linearly, a similar method[6] can be adopted even in the general case, the solution being again expressible as the sum of two Bessel functions if we neglect the square of the wavelength.

7. SUMMARY

Experimental studies reveal that when a collimated pencil of light is incident obliquely on a heated plate in contact with air, the field of observation exhibits a dark region adjacent to the plate into which the incident radiation does not penetrate, followed by a layer in which there is an intense concentration of light and then again by a series of dark and bright bands of progressively diminishing intensity. Photographs of these features have been obtained and are reproduced in the paper. The observed facts find a satisfactory explanation when the problem is considered from the standpoint of wave-theory and more completely on the basis of a formal analytical treatment. The optical characters of the mirage are observed to stand in the closest relation to the wave-optical phenomena referred to, changing with

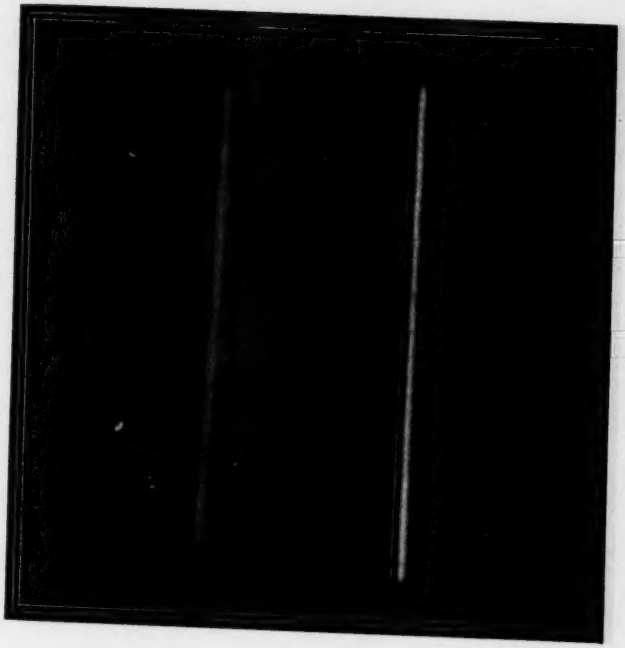

FIG. 1

FIG. 2

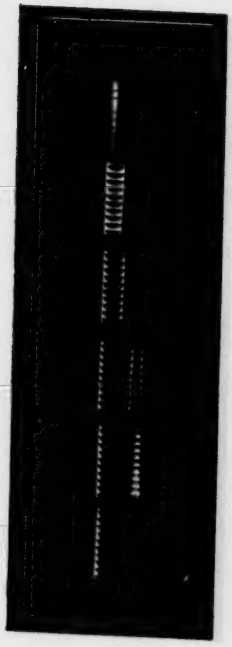

FIG. 3

the position of the observer's eye in the field of interference. The explanations of the mirage usually given are thus seen to be inadequate and unsatisfactory.

8. References

1. Minnaert, M. .. *Light and Colour in the Open Air*, G. Bell and Sons, London, 1940, Plate V.
2. Wood, R. W. .. *Physical Optics*, The Macmillan Co., New York, 1911, Plate III.
3. Epstein, S. .. *Proc. Nat. Acad. Sci.*, U.S.A., 1930, **16**, 628.
4. Planck, M. .. *Theory of Light*, Macmillan and Co., London, 1932, 204.
5. Hiller, W. .. *Phys. Zs.*, 1913, **14**, 718; 1914, **15**, 303.
6. Morse and Feshbach .. *Methods of Theoretical Physics*, McGraw-Hill, 1953, Part II, 1096.

ELECTRICAL OSCILLATIONS IN A D.C. GLOW DISCHARGE

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Recent experiments[1, 3–5, 8] have revealed the existence of oscillations in the electrical parameters and the light intensity of a D.C. glow discharge under a wide range of experimental conditions. Leaving aside the oscillations of the relaxation type[9] whose frequency shows a dependence on the circuit parameters the oscillations observed are mainly of two types, (1) plasma oscillations in the H.F. region (*Mcs.*) of the type observed for example by Langmuir and Tonks,[10] (2) oscillations observed in the L.F. (*Kcs.*) region generally associated with moving striations.[9] Both these types have been shown to include oscillations with single or multiple frequencies (with or without a background of continuous bands known as electrical noise). It is clear that any theory of the self-maintained discharge has to take into account the contribution of these oscillations to the maintenance and/or the economy conditions,[11] in the cathode dark space. The experimental results point to a great complexity in the mechanisms shown for example by the different relationships observed between the frequency of the oscillations and the experimental parameters of the discharge like i and p, the discharge current and the pressure respectively. The conditions for the occurrence of the oscillations (of the second type) observed by the different investigators emphasise again the complex nature of the phenomenon. A mechanism has been suggested by Donahue and Dieke[3] for these oscillations involving moving striations in terms of an electron trap formation in the negative glow of the D.C. discharge. Labrum and Biggs[5] have indicated the possibility of linking up the phenomenon of such coherent plasma oscillations (or waves) with that of electrical noise in the L.F. region. As has been already mentioned the experimental evidence shows that in many cases the frequencies observed are not single but consist of groups lying in different frequency ranges.

The above results prompted us to make a detailed study of the electrical oscillations in a D.C. discharge with a view to investigate, (1) the manner in which the frequency of the oscillations depends on i and p, (2) the connection between the different frequency groups and (3) the extent to which the phe-

nomena in the cathode dark space are affected when electrical oscillations are present in the discharge tube.

§ 2. Experimental

The discharge tube used was 35 mm. in diameter and was provided with an aluminium cathode. The anode was kept in a side tube so that the cathode ray beam, when it is formed, does not influence the processes in the anode region. The observations were taken for a cold cathode discharge in hydrogen with a pressure range of 40 to 200 microns, discharge voltages 0·6 to 11·2 kV., and discharge currents 0·1 to 2·5 m.a. The discharge voltage was obtained from a half-wave rectified circuit with filters giving an output in which the ripple was not greater than one per cent. (A preliminary investigation in which observations were taken with the H.T. voltage having values of the ripple percentage greater than the above showed that the ripple had no effect on the frequencies of the oscillations observed.) The positive terminal of the H.T. was connected to the anode; the cathode was earthed through a milliammeter. The H.T. voltage was measured by the usual method of observing the potential difference across a part of a series of resistors (having a total of 52 M. Ω) in parallel with the discharge tube. Gas streaming was used, directed from the anode to the cathode in order to obtain stable discharge conditions. The observations of Pupp[1b] show that the gas streaming has but an insignificant effect on the frequency of the electrical oscillations. The electrical oscillations in the L.F. region (Region I) were observed with a C.R.O. by tapping the potential across a variable resistor in the earth circuit. The H.F. oscillations in region II were observed with an absorption wavemeter (range 170 Kc./sec. to 70 Mc./sec.) and an insulated rectangular capacitor probe pick-up (30×7 mm.). This method of coupling was found to be quite sensitive and had the advantage that it enabled one to follow the H.F. oscillations in the different regions of the discharge. For some observations confirmatory readings were also taken with the probe and a (vacuum tube voltmeter) V.T.V.M. (having a frequency range of 20 Cs./sec. to 1 Mc./ sec.). The potential drop developed across a resistor of 22 M.Ω between the probe and earth was made use of, for the measurement by the V.T.V.M. The range of the V.T.V.M. overlapped those of the C.R.O. and the wavemeter and enabled the observation of the whole range of frequencies by a single instrument. In certain observations where the frequency of the oscillations varies rapidly with the experimental parameters, it becomes more convenient in these cases to follow them with the V.T.V.M. than with the wavemeter. The pressure in the discharge tube was measured with a Pirani gauge.

§ 3. THE EFFECT OF THE OSCILLATIONS ON THE CHARACTERISTIC OF THE DISCHARGE TUBE

The V–i characteristic of the discharge tube in the glow discharge stage is predominantly determined by the processes occurring in the cathode dark space. An estimate of the extent to which these processes are affected can be made by observing the change in the V–i characteristic, if any, at the stage when electrical oscillations set in. It has been observed by us in agreement with Pupp[1a] and Donahue and Dieke,[3] that there is a cut-off value i_c for the discharge current i beyond which no oscillations occur. The value of i_c as will be seen later is determined by the pressure p. We have therefore determined the characteristics for different values of p in the range 186 to 45 microns to observe if there is any change in the characteristic at the corresponding values of i_c. Small but definite changes for values of p in the range 50 to 80 microns only have been observed. For other values of the pressure the change is insignificant. That the presence of electrical oscillations should affect the V–i characteristic, of the D.C. discharge, is shown by our observation of the characteristic when an external R.F. signal (45 volts, 500 Kc./sec.) is superposed on the D.C. voltage. It was observed that when this is done there is always a momentary increase in the D.C. current and a corresponding decrease in the voltage across the discharge tube. Whereas the current falls slowly to its original value a part of the decrease in the H.T. voltage persists as a permanent effect of the imposition of the R.F. signal. The type of fluctuations described above have also been observed at the onset of the internal electrical oscillations in the discharge tube. Anticipating a result described later in the paper, it may be pointed out that the amplitude of the electrical oscillations has been shown to have a maximum value for the pressure range 60 to 90 microns. The effect of the oscillations on the characteristics are therefore expected to be significant for this range of pressures, which has been observed. There is evidence from the study of the radial distribution of the light intensity in the discharge channel with z, the distance from the cathode obtained in this laboratory by D. V. Nagamani (unpublished work) that the electrical oscillations when present affect the processes occurring in the cathode dark space. We have also been able to show (*vide* pp. 273 and 274) that the electrical oscillations are present in the cathode dark space when they are produced in the discharge tube. Warren[6] has observed however that the electrical oscillations do not affect the distribution of the electric field in the cathode dark space and hence the processes occurring in this region. This result is remarkable in view of the experimental evidence obtained by us. It would be interesting to investigate the conditions under

which the electrical oscillations fail to affect the region of the cathode dark space.

The characteristics obtained by us have a positive slope. The existence of electrical oscillations under these conditions confirms Pilon's[8] result—that the nature of the characteristic whether positive or negative has no effect on the conditions necessary for their occurrence. The previous observation in the field by Pupp[1a], Fox or Donahue and Dieke[3] were obtained for discharge with a negative characteristic.

§4. Variation of f the Frequency of the Oscillations with i and p

The frequencies of the electrical oscillations in region I were found to be in the range 40 to 100 Kc./sec. The oscillations were coherent, but also had on some occasions a background perhaps due to electrical noise. We were able to observe a pure sine wave pattern for the coherent oscillations in a majority of cases; only in a few cases the presence of harmonics (similar to the results of Pupp[1a]) was indicated. We were not able to confirm the result of Donahue and Dieke[3] that these oscillations occur only for certain discrete values of i. The frequencies in this region show only a relatively small variation with i and p as can be seen from the table of observations (Table I).

These frequencies are very much higher than those observed by Donahue and Dieke[3] but are of the same order as found by Pupp.[1a] The reason for this difference may very well be in the different experimental conditions used by these authors. The results of Pupp[1a] were obtained for a discharge in the rare gases He, Ne, Ar, Kr (pressures 500 to 5,000 microns) and i varying from 0·5–15 amp. The frequencies observed by him were in the range 30 to 400 Kc./sec. Donahue and Dieke,[3] on the other hand, observed the electrical oscillations in a sealed cold cathode discharge tube containing Argon at pressures 2·1 to 30 mm. of Hg and currents between 0·1 to 60 m.a., when frequencies lying in the range 1–5 Kc./sec. were observed. The frequencies observed by Donahue and Dieke[3] were found to be very sensitive to i whereas Pupp[1a] showed that they are essentially independent of i, but show a dependence on p and the nature of the gas. The results given above therefore represent oscillations which approximate more to those observed by Pupp rather than by Donahue and Dieke.

The frequencies observed simultaneously in region II with the wavemeter and the probe are shown in Table II.

TABLE I

Discharge in hydrogen

p microns	H.T. kV.	i m.a.	i_e m.a.	f Kc./sec.	Relative amplitude	Remarks
129	0·6	0·10		68	1·3	
	0·7	0·15	0·33	89	1·0	
	0·7	0·20	±0·07	85	1·2	
	0·7	0·25		89	0·6	
99	0·8	0·10		64	1·2	
	0·9	0·15		64	2·6	
	0·9	0·20	0·39	87	1·9	
	1·0	0·25	±0·09	39	2·3	Harmonics
	1·0	0·30		53	1·0	present
80	1·0	0·10		61	1·4	
	1·2	0·15	0·44	64	2·8	
	1·2	0·20	±0·03	94	1·6	Harmonics
	1·3	0·25		43	2·8	present
73	1·4	0·10		44	1·7	
	1·5	0·15	0·50	63	2·6	
	1·5	0·20	±0·11	93	1·6	
	1·6	0·25		79	0·8	
66	1·7	0·10		59	1·0	
	1·8	0·15		71	2·1	
	2·0	0·20	0·50	86	1·6	
	2·1	0·25	±0·04	91	0·9	
	2·2	0·30		93	0·5	
54	2·9	0·10	0·46	62	1·1	
	3·3	0·15	±0·01	81	1·0	
	3·5	0·20		91	0·8	

TABLE II

Discharge in Hydrogen

ρ microns	H.T. kV.	i m.a.	f_1 Kc./sec.	f_2 Kc./sec.	f_3 Kc./sec.	f_4 Kc./sec.	i_c m.a.
129	0·6	0·10	190 (9)	600 (1)	..	..	
	0·7	0·15	..	630 (1)	1020 (1)	..	
	0·7	0·20	185 (28)	500 (8)	870 (5)	..	0·33
	0·7	0·25	315 (34)	525 (5)	720 (6)	..	±0·07
	0·8	0·30	..	570 (7)	1200 (5)	..	
99	0·8	0·10	250 (10)	510 (1)	690 (1)	1200 (1)	
	0·9	0·15	..	510 (6)	800 (5)	..	
	0·9	0·20	..	540 (11)	750 (10)	..	0·39
	1·0	0·25	185 (42)	550 (15)	900 (12)	..	±0·09
	1·0	0·30	340 (42)	725 (15)	1750 (1)	..	
80	1·0	0·10	205 (13)	600 (3)	850 (2)	..	
	1·2	0·15	270 (18)	570 (8)	810 (7)	1300 (5)	
	1·2	0·20	..	540 (11)	750 (10)	..	0·44
	1·3	0·25	180 (42)	500 (16)	870 (12)	..	±0·03
	1·4	0·30	250 (52)	620 (18)	1750 (1)	2100 (1)	
73	1·4	0·10	280 (10)	520 (3)	655 (2)	810 (1)	
	1·5	0·15	340 (19)	590 (7)	950 (6)	..	
	1·5	0·20	..	570 (11)	860 (9)	..	0·50
	1·6	0·25	185 (43)	550 (17)	975 (13)	..	±0·11
	1·7	0·30	260 (55)	680 (20)	1850 (2)	2300 (1)	
66	1·7	0·10	..	525 (4)	710 (3)	..	
	1·8	0·15	320 (18)	650 (6)	960 (5)	..	
	2·0	0·20	..	650 (10)	1150 (8)	..	0·50
	2·1	0·25	184 (45)	540 (12)	880 (10)	..	±0·04
	2·2	0·30	275 (51)	710 (16)	1700 (1)	..	
60	2·0	0·10	180 (10)	520 (1)	700 (1)	..	
	2·2	0·15	..	510 (6)	710 (5)	1300 (2)	
	2·4	0·20	..	740 (6)	..	..	0·49
	2·7	0·25	185 (45)	530 (12)	930 (9)	..	±0·03
	2·8	0·30	295 (50)	710 (13)	..	..	
48	3·8	0·10	240 (3)	..	..	..	
	4·0	0·15	..	650 (2)	..	..	
	4·2	0·20	195 (30)	565 (5)	1050 (2)	..	0·45
	4·6	0·25	235 (38)	630 (7)	..	..	±0·00
	4·7	0·30	325 (47)	840 (7)	..	..	

It should be pointed out that the frequencies and their amplitudes (as given by the peak current in the wavemeter which are given in brackets in Table II) are found to show fluctuations with time for which the discharge is passed, an observation in agreement with that of Donahue and Dieke.[3] The observations given in the table refer to the average conditions and represent a typical set.

Figure 1 shows the variation of f with i in both the regions I and II. The results show that whereas mono-frequency oscillations are observed in region I, for a given i, there exist a group of frequencies (usually about 3) in region II. These different frequencies probably correspond to the different modes with the correspondingly different frequencies, observed by Donahue and Dieke.[3]

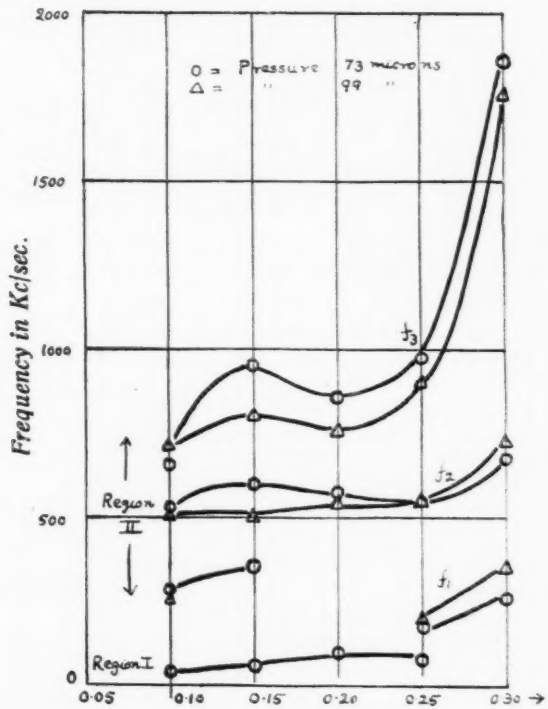


FIG. 1. Variation of f with i.
O → p = 73 microns and Δ → p = 99 microns.

This correlation appears to be supported by the variation of the frequency in this region with i. One observes for example the existence of discontinuities in the f-i curve showing that the frequencies are absent for certain values of i. On the other hand in contrast to their observations the frequencies f_1, f_2, f_3 of the various modes observed by us show different degrees of dependence on i. The discontinuities are observed for mode I, the second mode shows only a small variation with i whereas the frequency f_3 of the third mode shows an extremely rapid increase with i. This type of variation agrees with the one found by Pilon[8] but is exactly opposite to what has been reported by Donahue and Dieke.[3] In their observations the frequency f was found to decrease with increase in i. These results indicated to us that the frequency of the oscillations may not be determined by i in a simple manner. The other parameter which may be expected to determine the frequency is the over-voltage. We have shown in Fig. 2 how the over-voltage varies with i for different values of the pressure used. The over-voltage has been taken to be equal to V (maintenance)–V (breakdown)

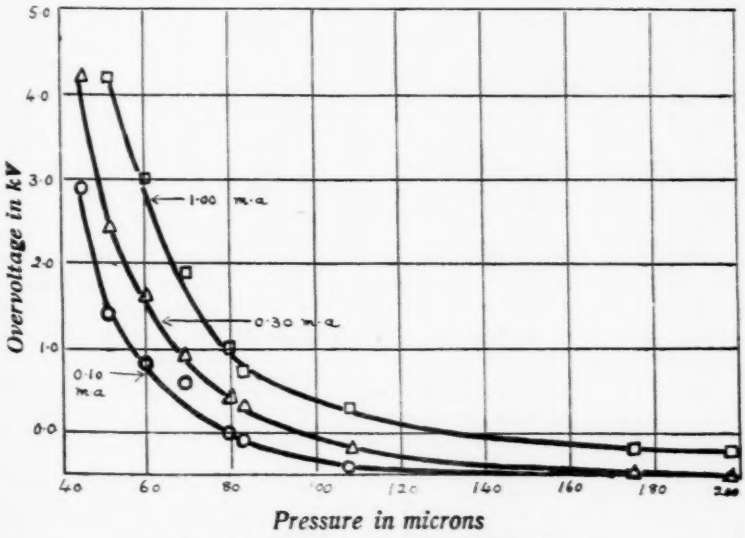


FIG. 2. Variation of over-voltage with p.
$i = 1{\cdot}00$, $0{\cdot}30$, $0{\cdot}10$ m.a.

corresponding to the different experimental conditions. We observe that the over-voltage at a given pressure decreases rapidly with the decrease in current. The over-voltage becomes zero and actually negative for the pressure in the range 80 to 200 microns whereas the range over which the oscil-

lations are most prominent is 60 to 90 microns. The observation indicates that the over-voltage is a significant parameter as far as the processes responsible for the electrical oscillations are concerned. The dependence of f on i is important from the point of view of the mechanism suggested by Donahue and Dieke for the occurrence of the moving striations.

In order to study the variation of f with p, a special set of observations was taken which is shown in Fig. 3. The variation of f with p in both the regions I and II is quite significant and also similar and shows that the frequency of the generated electrical oscillations has a minimum value for a certain value of p generally in the range 60 to 90 microns for the frequencies belonging to both the regions (including the different modes).

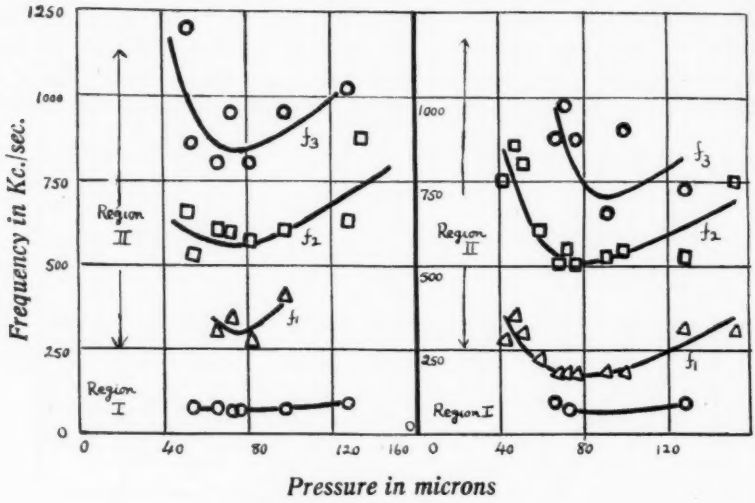


FIG. 3. Variations of f_e with p.
$i = 0{\cdot}15$, $0{\cdot}25$, m.a.

§ 5. VARIATION OF THE CUT-OFF i_c WITH p

The cut-off current i_c beyond which no electrical oscillations are obtained has been found by us to be identical for the frequencies in both the frequency regions (including the different modes). As in the case of frequencies, i_c is also observed to be very sensitive to the conditions of the discharge and to the time for which the discharge is passed. The values of i_c given (Fig. 4) as a function of p represent the average of a very large number of observations. The probable error in the measurement of i_c has been indicated in the figure.

It is more convenient to measure i_c with the V.T.V.M. than with the wavemeter. A set of confirmatory observations taken with the V.T.V.M. are shown in Table III. It should be pointed out that the V.T.V.M. readings give the resultant of the various frequency components (having possibly different phases). This consideration should not affect the determination of i_c with the V.T.V.M. as it has been shown by independent observations that i_c is the same for all frequencies.

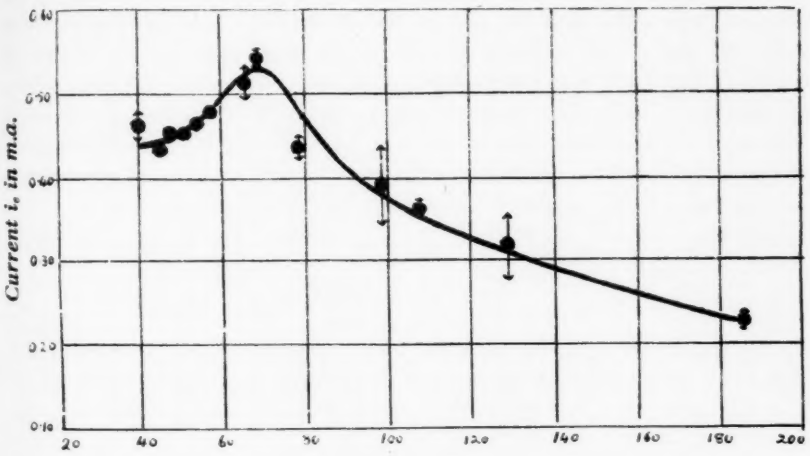


FIG. 4. Variation of i_c with p.

TABLE III

Discharge in hydrogen variation of i_c *with* p (*with V.T.V.M.*)

Pressure microns ..	173	129	91	76	71	62	60	48	43
i_c (m.a.) ..	0·20	0·30	0·35	0·41	0·45	0·47	0·46	0·45	0·45

Both these observations bring out the remarkable result that i_c is a maximum for the same pressure range for which f shows a minimum. Pupp[1a] had observed that i_c decreases with p in an almost linear manner. Considering the fact that the pressures used by him were in the range 500 to 5,000 microns, the results reported in this paper show approximately the same type of variation for large values of the pressure.

The various frequencies observed have the same cut-off i_c, vary with the pressure in a more or less similar manner but show a widely different

dependence on i. These observations enable one to conclude that the electrical oscillations belonging to these various frequencies are definitely related to one another but do not arise from a common mechanism.

§ 6. VARIATION OF THE AMPLITUDE OF THE ELECTRICAL OSCILLATIONS WITH i AND p

If one observes the variation of the amplitude of the oscillations (directly, in the C.R.O. range, and by measuring the peak current in the case of the wavemeter) as a function of i and p, one finds that it is a maximum for one value of i and p. Since the amplitude of the oscillations has to be zero for $i = 0$ and also for $i = i_c$ it is clear that it must have a maximum for an intermediate value of i. The observations in Table IV show that the value of i for which the amplitude is a maximum is not the same for the oscillations in regions I and II. This observation again emphasises the essential differences in the behaviour of the different frequencies with i.

TABLE IV

Discharge in hydrogen

($p = 66$ microns)

i m.a.	V.T.V.M. (reading)	Wavemeter peak current μ/a.	C.R.O. μa.
0·05	50	..	..
0·10	76	4	1·0
0·15	91	6	2·1
0·20	94	10	1·6
0·25	90	12	0·9
0·30	78	16	0·5
0·35	69	..	..
0·40	54	..	..
0·45	40	..	..
0·46	0	..	..

The variation with p shows that the amplitude is a maximum for p in the range 60 to 90 microns which is the same range for which f is a minimum and i_c is a maximum.

§ 7. Space-Charge Density in the Cathode Dark Space

At this stage it will be appropriate to introduce another parameter of the discharge ρ, the net space-charge density in the cathode dark space. It has been shown,[7] that the electric field E in the dark space varies with z, the distance from the cathode according to the relation:

$$\mathrm{E} = c\,(d - z) \tag{1}$$

c = constant, d = length of the cathode dark space. The space potential V will vary with z according to the relation:

$$\mathrm{V} = cdz - \frac{cz^2}{2}$$

since $\mathrm{V} = 0$ at $z = 0$. Assuming that for $z = d$, $\mathrm{V} \sim \mathrm{V}_0 =$ applied H.T.

$$\mathrm{V}_0 = \frac{cd^2}{2} \qquad \text{or} \qquad c = \frac{2\mathrm{V}_0}{d^2}\,. \tag{2}$$

Assuming the field in the dark space to be a space-charge one, it can be shown from Poisson's equation that ρ the positive space-charge density is constant in the cathode dark space and has the value:

$$f = \frac{c}{4\pi} \sim \frac{2\mathrm{V}_0}{4\pi d^2}. \tag{3}$$

Table V gives the value V_0/d^2 as a function of p.

One observes that V_0/d^2 which is a measure of ρ has a minimum value for p in the same range 60 to 90 microns for which i_c is a maximum. This result indicates that there is a close relationship between the oscillations and the processes occurring in the cathode dark space.

§ 8. Variation of the Amplitude of the Electrical Oscillations with z, the Distance from the Cathode

Figure 5 gives the relative variation in the amplitude of the electrical oscillations in the different regions of the discharge as measured with the capacitor probe and the wavemeter (and the V.T.V.M.). For this purpose the probe was mounted on a Vernier stand and then moved parallel to the discharge tube. The distance of the probe from the discharge tube was kept constant at 2 mm. Curves A and B represent the results obtained with the wavemeter and the V.T.V.M. under the same conditions. For the sake of

TABLE V

Discharge in hydrogen

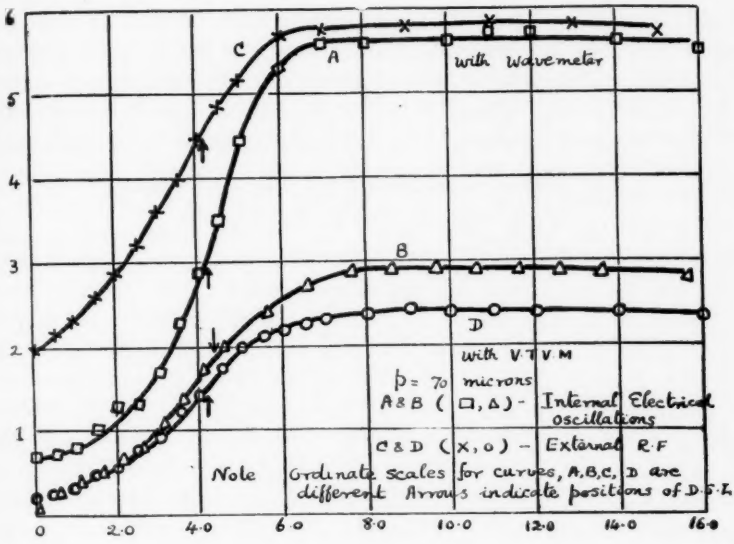
(Current = 1·0 m.a.)

p microns	V_0 kV	d mm.	V_0/d^2 Volt/mm.
186	0·9	19	2·5
129	1·1	25	1·8
108	1·3	28	1·7
99	1·5	30	1·7
73	2·6	40	1·6
69	2·7	43	1·5
66	3·3	45	1·6
60	4·2	50	1·7
54	5·4	55	1·8
48	7·2	60	2·0
45	8·1	63	2·0
40	11·2	69	2·4

comparison we have observed the variation when no internal oscillations are present but an external R.F. signal (45 volts, 500 Kc./sec.) from a Hartley oscillator is superposed on the D.C. at the anode through a vacuum condenser. Curves C and D represent the results obtained with the wavemeter and the V.T.V.M. respectively for this case.

The distribution of the amplitude of the oscillations follows more or less that of the D.C. space potential in the different regions of the discharge. The course of the curves in the cathode dark space—the positions of the length of the cathode dark space are shown by the arrows in Fig. 5—are what we might have expected on the basis of those obtained for the distribution of potential in the region by the electron beam method.[7] The existence of the electrical oscillations in the cathode dark space is very clearly

shown thus confirming the results of Donahue and Dieke[3] which were obtained however by measuring the intensity of light.



z *in cms.*

FIG. 5. Variations of the amplitude of the electrical oscillations with z, the distance from the cathode.

A and B → Internal Oscillations.
C and D → External R.F.
$p = 70$ microns.
A and C → With wavemeter.
B and D → With V.T.V.M.

It was observed by them that the percentage change in the amplitude of the intensity oscillations of the light of the discharge glow was very much greater than that observed either in the current or the voltage. This parameter was therefore chosen to follow the course of the oscillations in the various regions of the discharge. The results reported here give a more direct confirmation for their observations and establish a new method for following the electrical oscillations in the different regions of the discharge.

The curves obtained for the internal oscillations and for the external R.F. signal are more or less the same. They are obviously determined by the parameters of the D.C. discharge. We have observed a marked difference in the two cases only in the anode region, *i.e.*, in the side tube. In the case

of the internal oscillations the amplitude falls to zero at the anode whereas in the case of the external signal, the amplitude shows an increase right up to the anode. The electric field except in the region of the cathode dark space due to the D.C. potential as compared with the R.F. is very weak. Taking into account this fact, one can conclude that the seat of the electrical oscillations is located somewhere in the negative glow region where its amplitude has a maximum. This observation agrees with the basic assumption of the mechanism proposed by Donahue and Dieke[3] for the oscillations.

§ 9. VISUAL APPEARANCE OF THE DISCHARGE WITH AND WITHOUT OSCILLATIONS

When no electrical oscillations are present in the discharge, a number of stationary sharp striations can be observed in the anode region in the side tube. When oscillations occur, the striations begin first to vibrate and then appear to coalesce so that the glow in this region has the appearance more or less of a uniform column. This is well shown by the microphotometer curves obtained for the light intensity in this region (1) with, (2) without oscillations. The same effect is observed when instead of an internal H.F., an external R.F. field is superposed in the manner described above. The observations pose the question whether the changes observed visually in the discharge *are produced by* the occurrence of electrical oscillations produced elsewhere, say for example, in the negative glow or that these changes represent the vibrations of the striations which produce the electrical oscillations. There is no doubt however that there is a close correlation between the striations and the electrical oscillations observed.

§ 10. DISCUSSION

As has been mentioned, the mono-frequency oscillations in the lowest frequency range have been ascribed to the moving striations. A mechanism has been recently suggested by Donahue and Dieke,[3] for these striations and therefore for the L.F. oscillations. Donahue and Dieke start their argument with the well-known result that the electrons coming from the cathode start ionisation by collision (and also excitation) from the end of the cathode dark space and the beginning of the negative glow; but do not have enough energy left to produce further ionisation by the time they traverse the length of the negative glow. The ionisation (and also excitation) must have a maximum somewhere between the limits of this region.

As the electric field in the negative glow is small, the process will lead to an accumulation of electrons at some place in the negative glow and therefore to the formation of an electron trap or a local space-charge field having

a direction opposite to that of the applied electric field. This should lead to a decrease in the cathode current and therefore affect the electric field in the cathode dark space and finally lead to the stoppage of the discharge. To avoid this, a positive striation is assumed to start from the anode (the exact mechanism for which is not given) which, when it draws near the electron trap in the negative glow, releases the electrons from the trap (which now move as a secondary negative striation towards the anode) and simultaneously starts a secondary positive one towards the cathode. The positive striation, when it moves through the cathode dark space to the cathode, causes an enhanced burst of electrons from the cathode by momentarily raising the cathode fall voltage. This burst travels away from the cathode as a new negative striation.

As the average velocity of the negative striation has been found[3] to be ($\sim 10^6$ cm./sec.) much greater than that observed for the positive striations ($\sim 6 \times 10^3$ cm./ sec.) a negative striation will meet several positive ones moving towards the cathode in the whole of the discharge space. Experimental evidence indicates however that the regions in the discharge, where the two striations meet, neutralise each other and form a plasma are fixed points in the discharge of which the location of the electron trap in the negative glow represents the most important one.

The instant when the two striations meet at any point in the discharge has been assumed to be the occasion for the maximum value for the light emission. The periodic striations moving through the discharge space constitute according to these authors the L.F. mono-frequency electrical oscillations observed. It has been pointed out[9] that the assumption of an electron trap and a subsequent reversal of the electric field in the negative glow is not supported by the observations of Warren[6] on the distribution of the electric field in both a normal and an abnormal type of discharge in the various gases (including air, hydrogen and argon) for pressures between 30 and 1,000 microns and $i = 0{\cdot}1$ to 10 m.a. He was not able to observe any reversal of the field in the negative glow or elsewhere as was observed by some of the earlier workers (*e.g.*, Stein[7] in nitrogen for pressure 50 to 400 microns, current 0 to 2 m.a.). The pressures used by Warren are very much smaller than the ones used by Donahue and Dieke or Pupp but they correspond to the pressures used by us for the observations reported in this paper. At the same time one has to remember that Warren was not able to find any effect of the electrical oscillations on the distribution of the electrical field in the dark space even when they were present, an observation which is not consistent with the observations of Donahue and Dieke or those reported in this paper.

At the same time it is not clear whether the creation of an opposing local space-charge field anywhere in the discharge, say for example, either in the negative glow or even in the positive column (where the striations occur) will always lead to the generation of the electrical oscillations.[5] Only an experimental investigation can supply the answers which will clarify both these points.

In terms of this mechanism on general considerations one should expect to find that the frequency of the oscillations should increase with increasing discharge current, as the current will determine the time required for the building up of the space-charge field in the electron trap. The observations of Donahue and Dieke, Pilon and those reported in this paper do not show such a simple relationship. Nor is there a simple explanation forthcoming for the existence of the cut-off current. Our observations on the over-voltage and the space-charge density in the cathode dark space show that the processes in this region play a significant part in the production of the oscillations. Our observations confirm however the basic assumption of Donahue and Dieke that the seat of the oscillations is the region of the negative glow (*cf.* pp. 273 and 274).

The behaviour of the various frequencies with the experimental conditions show as has been already mentioned that they are related with one another but do not arise out of a single common mechanism. In this connection it would be interesting to recall a mechanism proposed by Labrum and Biggs[5] for the production of electrical noise in the discharge tube. Starting with their observation that the striations and the coherent oscillations always appear together, they assume these oscillations to be plasma waves and the striations to be due to the stationary wave pattern formed by these waves, with the result that space potential maxima and minima are produced in the region of the striations. A Barkhausen-Kurz type of oscillations of the electrons and the ions can take place about the potential maxima and minima, respectively leading to the production of H.F. and the L.F. electrical noise. The observation that coherent oscillations are not always accompanied by electrical noise is explained by assuming that the potential maxima or minima built up by the striation alone are not of a sufficient magnitude but require the added presence of a constriction to boost it up to the required magnitude necessary for the generation of these oscillations. The interruption of the oscillations of the electrons and the ions on account of collisions with the gas atoms can lead to oscillations with a continuous frequency spread as shown by these authors. This would locate the seat of these oscillations in the positive column. The secondary oscillations therefore

are assumed to be dependent on the building up of potential maxima and minima by the primary coherent oscillations. It is possible that an interrelation of a similar type may exist between the various groups of frequencies observed by us.

We thank Dr. R. K. Asundi for useful discussions and suggestions.

§ 11. Summary

The phenomenon of electrical oscillations in the case of a D.C. discharge in hydrogen in the region of the positive V-*i* characteristic has been investigated for the pressure range 40 to 200 microns, discharge voltages 0·6 to 11·2 kV. and discharge currents 0·1 to 2·5 m.a.

Coherent oscillations were observed in the frequency range 40 to 100 Kc./sec. which were accompanied by three or four frequency groups in the range 170 to 2,300 Kc./sec.

1. The existence of a common cut-off current for all these frequencies has been shown which is found to depend on the pressure in such a manner that it has a maximum value for $p = 60$ to 90 microns.

2. The frequencies of the oscillations show a significant dependence on i and p and are independent of the circuit parameters. The frequencies have a minimum value for $p = 60$ to 90 microns. The lower frequencies show only an insignificant variation with i whereas in the highest frequency group there is a very rapid rise of frequency with current.

3. The amplitude of the oscillations is determined by i and p and shows a maximum for some value of i and $p = 60$ to 90 microns.

4. The variation of the amplitude in the different regions of the discharge indicate that the seat of the oscillations is in the negative glow.

5. The processes in the cathode dark space have been shown to have a significant effect on the electrical oscillations.

References

1 *a*. Pupp, W. .. *Phys. Zeits*, 1932, **33**, 844; 1935, **36**, 61.

1 *b*. ———— .. *Ibid.*, 1934, **35**, 705.

2. Fox, G. W. .. *Phys. Rev.*, 1931, **37**, 815; 1930, **35**, 1066.

3. Donahue, T. and Dieke, G. H. *Ibid.*, 1951, **81**, 248.

4. Stewart, A. B. .. *J. Applied Physics*, 1956, **27**, 911.
5. Labrum, N. R. and Biggs, E. K. *Proc. Phys. Soc. Lond.*, 1952, **65 B**, 356.
6. Warren, R. .. *Phys. Rev.*, 1955, **98**, 1650.
7. Stein, R. P. .. *Ibid.*, 1953, **89**, 134.
8. Pilon, A. M. .. *Ibid.*, 1957, **107**, 25.
9. *Handbuch Der Physik* 1956, **22**, 140 and 187.
10. Tonks, L. and Langmuir, I. .. *Phys. Rev.*, 1929, **33**, 195.
11. *Handbuch Der Physik* 1956, **22**, 143.

POLARISATION AND POLISHING STUDIES ON COPPER IN A HULL CELL

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Abstract

In continuation of our previous work,[1-2] the effects of polishing time, sp. gr. of the electrolyte, addition of EDTA, electrolyte level, etc., on the position, size and shape of the variously polished bands obtained in a Hull cell have now been studied. I–V measurement when carried out showed that total cell voltage increases regularly with total cell current, thereby affording no explanation for the variously polished bands. However, with a specially designed probe electrode,[3] it has been possible to study the current distribution as existing during polarisation at different points of the anode surface and thus offer some explanation for the appearance of variously polished bands which could not be interpreted earlier in terms of electrode potentials.

Introduction

In recent times, various attempts both theoretical and practical have been made to work out the design and the mathematical treatment of various types of cells which would give a uniformly varying current density along an electrode and thereby facilitate and expedite the study of the effect of variables in electrodeposition and polishing processes. Hull[4] designed his cell primarily for plating studies which have been reviewed by Cuthbertson.[5] A mathematical treatment of the various types of cells has been given by Skwirzynski and Huttly.[6] Lorking,[7] for the first time, used the Hull cell for polishing studies on copper in orthophosphoric acid and found that highly different finishes are produced on the anode. Further, there are not only sharp contrasts and discontinuities between these finishes or bands, but two well-polished bands are separated by a small unpolished band.

Various workers[8-12] have reported their experimental and theoretical findings on the mechanism of electropolishing of copper in orthophosphoric acid solution, the nature of the film formed on copper during polishing, and other aspects of allied interest. But so far no explanation for the above

effect, observed by Lorking, has been offered by anyone. Some of our attempts in this connection have already been reported.[1-2] Further studies seeking to explain the above phenomena and also some experimental results of general importance on the electrolytic polishing of copper in a Hull cell are reported below.

THE HULL CELL

The cell used in the present study is made of perspex and conforms to the specifications as given by Hull[4] with inclined side as the anode. The pretreatment and preparation of anode and cathode plates of high-conductivity copper (purity 99·98%) are already described in our previous paper.[1] The cell is operated from a constant direct voltage source. A 50% (by volume) solution of orthophosphoric acid (B.D.H. L.R. quality, sp. gr. 1·75) in distilled water has been used as electrolyte and the made-up solution (sp. gr. 1·38) contains 756 g./l. of phosphoric acid.

OBSERVATIONS

(1) *Effect of polishing time on the position and size of the various polished regions*

It is generally believed that an increase in the time of polishing would merely change the reflectivity and the general appearance of a polished region and would produce no change in its position with respect to other regions. On the contrary, it is experimentally found that as reported in the case of hyperbolic cells,[2] polishing time has a profound effect on the position and size of the various regions when copper is electropolished in a Hull cell. Further these bands are regularly reproducible and thereby lend themselves to a systematic study.

The different polished regions are found to move towards the low current density end of the anode as the polishing time increases while the total cell current is kept constant. But this shifting of the regions is found to continue only up to a certain definite time, after which the regions are found to retrace towards the high current density end of the plate. For instance, while polishing at a total cell current of 4 amps., the shifting of the bands towards the low current density end was found to occur in one direction upto a time of about 8 minutes. But after 8 minutes, the shifts were in the opposite direction as the time of polishing increased. It should be mentioned here that the distance, through which a band shifts towards the low current density end during a certain interval of time, is much larger than the shift experienced by the same band for the same increase in polishing

time while retracing towards the high current density end. A typical example of the effect of electrolyte level and polishing time is shown in Fig. 1.

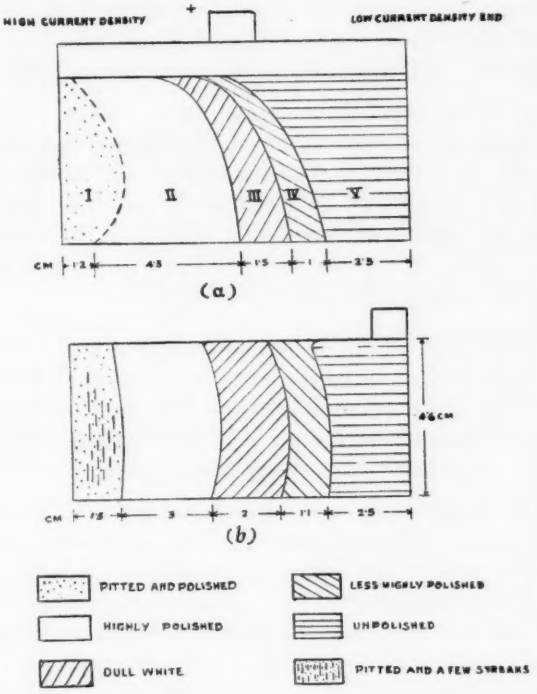

FIG. 1. Effect of polishing time and electrolyte level on the size and shape of bands.
(*a*) 4 A, 3½ mts., anode not wholly immersed.
(*b*) 4 A, 5 mts., anode wholly immersed.

(2) *Effect of EDTA*

Unlike the influence of surface active agents which have been studied by Lorking,[7] the effect of complexing agents was not so far known. Hence, a few trials were made with 1 oz./gal. of ethylene-diamine-tetra-acetic acid disodium salt (briefly termed EDTA). Although EDTA does not normally form complexing ions in highly acidic solutions yet during polishing the pH may actually rise considerably at the electrode surface. But in our trials EDTA showed no perceptible effect on the reflectivity, structure, colour, etc., of the different electropolished regions.

(3) *Effect of sp. gr. of the electrolyte on electropolishing*

The reason why increasing viscosity is presumed to improve the capacity for polishing have already been discussed by Walton,[13] *e.g.*, copper is not polished in a sulphuric acid electrolyte, but becomes polished if glycerol is added.[14] It also explains that increase in dilution and temperature generally hinder the polishing of copper in orthophosphoric acid.[15]

The sp. gr. of the solution was varied from 1·73 to about 1·15. It is found that as the sp. gr. increases (i) the whole plate gets more or less polished, (ii) but the polishing is very poor in quality, (iii) the highly polished region shifts towards the low current density end and as the sp. gr. decreases the unpolished region extends in area. The sp. gr. of the electrolyte suitable for studying the different regions seems to be about 1·4 corresponding to a concentration of about 760 g./litre of H_3PO_4.

(4) *Effect of level of electrolyte*

As it was felt that the curvature of the bands might be due to edge effect coupled with hydrodynamic factors depending on the level of the fluid electrolyte with respect to the top edge of the anode, some experiments were carried out with different electrolyte levels.

(i) *Solution level well above the edge of the anode.*—Different levels were tried and in one particular experiment, the level of the electrolyte was about 1·3 cm. above the plate edge (volume of solution used being 320 c.c.) so that the plate was completely immersed. In this as well as in all the following experiments, the anode was well illuminated by a powerful beam of light (concentrated arc lamp, Sylvania Electric Corporation) so that the polishing effects could be observed clearly as time of polishing increases. The following changes were noticed in the above experiment.

As soon as the current (4A) is switched on, the band that appears at the high current density end of the anode is seen to be curved at the top towards the low current density end, contrary to what is usually observed when the plate is not completely immersed. After 30 seconds the same band is found to have moved and occupied about $\frac{1}{3}$ area of the plate. In 1 minute the band has extended up to half the plate and it is still curved towards the low current density end. After 1 minute, the blue thick layer can be seen descending down the plate. In 1 minute 15 seconds, a fresh white band appears at the high current density end where the solution starts getting turbid with gas bubbles and loosened white particles. At 2 minutes the curvature towards low current density end of the first bright band which has now moved up to $\frac{2}{3}$ length of the plate is found to be getting less and less but still in the

same direction. In 3 minutes the first band is almost straight but with a tip (I') bent towards the low current density end and the white band which has now extended up to about 1 cm. is curved slightly towards the high current density end both at the top as well as at the bottom. After 5 minutes of polishing, the solution becomes turbid. Due to poor visibility, further polishing was discontinued. The details on the plate after 5 minutes of polishing may be seen in Fig. 1 (*b*).

(ii) *Anode just flushed.*—As exact flushing is not practically possible, a few trials were made by having the solution level as close to the anode edge as possible. For example, in one experiment, the solution level was less than 2 mm. above the plate edge and the volume of solution required for this was 267 c.c. In this experiment, it was found that as soon as polishing starts, the bright band that appears at the high current density end is very straight and it remains so up to a period of about 40 seconds, during which it extends up to middle of the plate. After 40 seconds, a slight curvature towards the high current density end appears in this band, with the simultaneous appearance of a white band at the high current density end. As time passes, the bands gradually curve more and more towards the high current density end while extending towards the low current density end.

(iii) *Solution level below the top edge of the anode plate.*—A number of experiments were conducted in which the solution level was varied from almost the flushing stage to about a height of 1·5 cm. below the plate edge and it was invariably found that in all cases the bands were curved towards the high current density end from the beginning to the end of the polishing operation.

It, therefore, appears that the curvature of the bands is quite a complex phenomenon and that it is more or less related to the electrolyte level, the edge effect, shorting of different potential regions through copper and the duration of polishing, along with the consequent changes introduced in the bath.

(5) *Total cell current* versus *total cell voltage*

Jacquet[14–16] has made some fundamental studies with regard to the polishing of copper in orthophosphoric acid. According to him, the curve of anode current-density *vs.* cell voltage $I = f(v)$, which is typical of the phenomenon of polishing, consists of four well-defined parts: (1) a straight line, along which the copper anode dissolves regularly without any visible gas evolution, (2) a region of unstable electrical characteristics in which the current decreases even on increasing voltage, (3) a horizontal portion

corresponding to an abrupt increase in cell voltage while the current remains nearly constant and (4) a sloping section in which the current increases very rapidly while the voltage increases relatively slowly and distinct evolution of gas occurs at the anode.

It is to be noted that Jacquet used a cathode (100 cm.^{2}) which was much bigger than the anode (2 cm.^{2}) and therefore the cathode reaction—liberation of hydrogen—would not interfere with the form of the curve.

Now the questions that naturally arise are these: (1) what would be the shape of the I–V curve in a Hull cell where the anode is nearly double the size of the cathode and where the cathode reaction cannot be ignored and further the anode is kept inclined with respect to the cathode, thereby producing a wide range of current distribution on the anode? (2) would the I–V curve of a Hull cell throw some light on the formation of variously polished bands?

With a view to answer the above questions, experiments were carried out in a Hull cell by varying stepwise the total cell current from 250 ma. to 6 amps. and recording the corresponding total cell voltage after 1 minute, at each step. The readings are graphically shown in Fig. 2. It is seen that the voltage increases regularly with increasing cell current and no abrupt or rapid changes take place either in current or voltage, as observed by Jacquet. Obviously, the I–V curve of the Hull cell offers no clue to the occurrence of variously polished bands and further the regular shape of such curves suggests that cathodic reaction does influence the anodic phenomena. In fact, Honeycombe and Hughan[15] have shown that if the area of a copper anode in a phosphoric acid electrolyte is increased until it is equal to that of the cathode, the horizontal portion of the $I = f(v)$ curve becomes less and less clearly defined. Moreover as the measured cell potential may be presumed to be an average value of the potentials of different anode bands having a more than 10-fold current variation from one end to the other, it is not surprising that I–V curves in Hull cell differ so much from ordinary cells.

(6) *A new probe electrode for comparative current density measurements*

Anode potential measurements in a Hull cell have been made and reported by us in our previous paper.[1] As it has been pointed out there, these potential studies do not help to explain the formation of differently polished bands and also why two well-polished bands are separated by a frittered region. It was, therefore, surmised that the clue to the interpretation of such phenomena could be found only by a macroprobe of current distribution in various

bands. A detailed literature survey was made but it did not reveal any simple and ready method of studying the current distribution as existing during polarisation at different points of the electrode. After initial trials a new probe electrode, the details of which appear elsewhere,[3] was evolved.

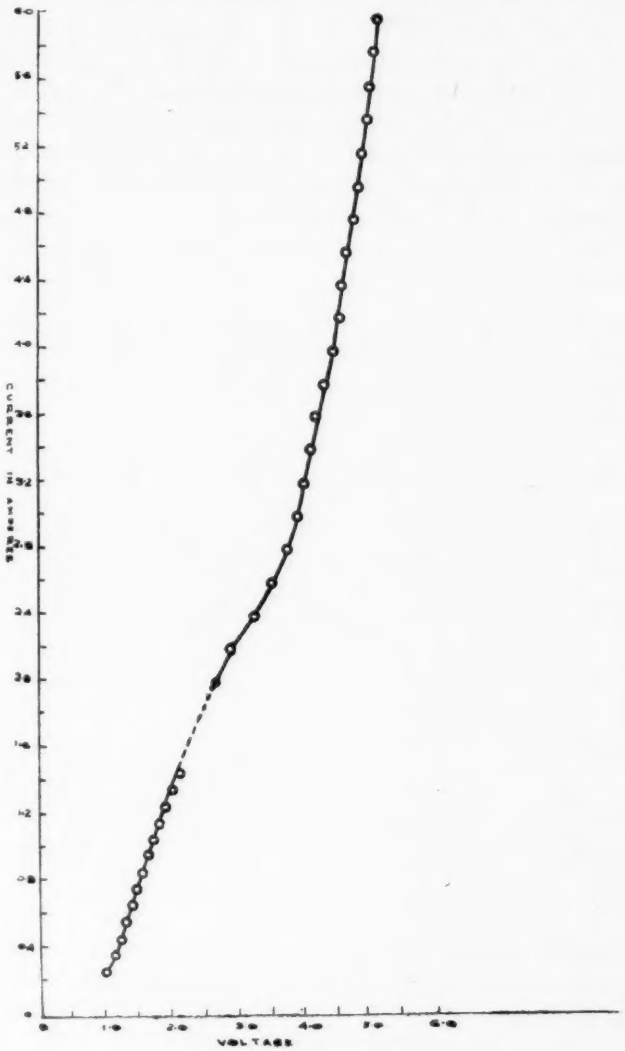

FIG. 2

With this new type of probe electrode, it has been possible to study the current distribution as existing during polarisation at different points of the anode surface.

(7) *Simultaneous measurement of current and potential along the anode plate for a fixed total cell current*

These were carried out using a probe electrode as described above for comparative current measurements and a Luggin capillary attached to a normal calomel electrode for potential measurements, both electrodes being kept separated by a small distance of about 1 mm. and suitably mounted on the stage of a travelling microscope so that the whole assembly could be moved parallel to the anode surface.

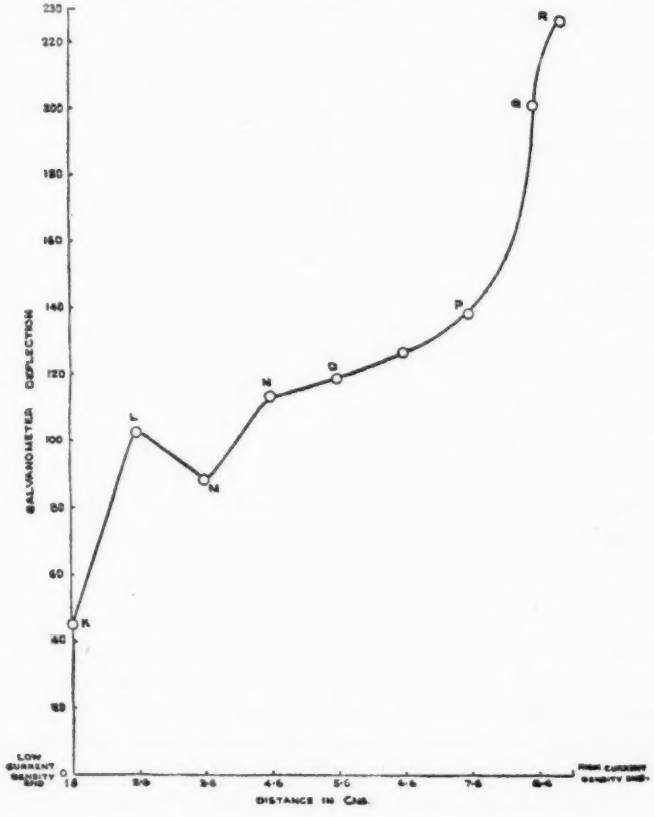

FIG. 3

Current and potential values corresponding to various points on the anode plate were noted. The values thus measured depend on many factors, such as the distance between the electrodes and the anode plate, the depth to which the electrode-tip is immersed in the electrolyte, the size of the capillary-tip or the loop of the probe electrode, composition of the bath, changing nature (with time) of anodic films in different regions, etc. As the measurements and the movements of the electrodes inevitably take time and slightly disturb the conditions, exact reproducibility of such readings becomes very difficult. However, they appear to be comparable. Figure 3 shows current distribution *vs.* distance along the anode and in Fig. 4 the potential variation with distance is plotted.

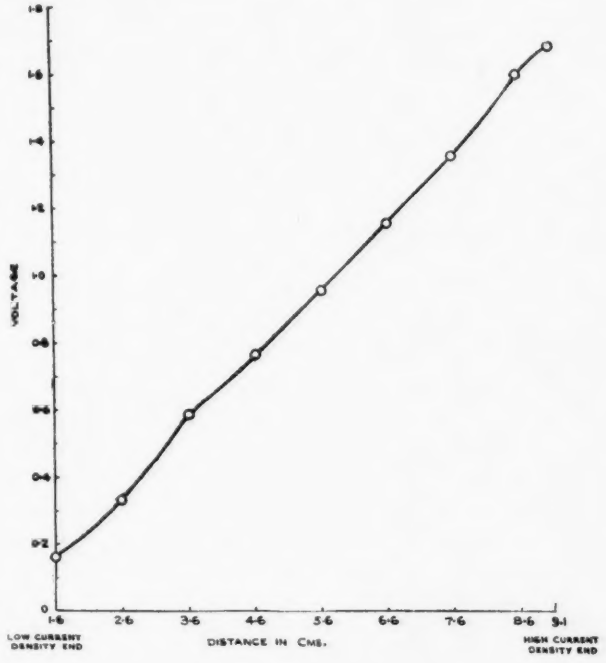

FIG. 4

The dull white region III on the electropolished sample (Fig. 1) is situated at a distance of about 3·6 cm. from the low current density end of the plate and it corresponds to the region round about the point M on the curve. The unpolished region (V) of the sample is represented by the initial portion of KL, the polished region IV by the curve around high current density point L

and regions II and I by portions near about N and up to OPQ. QR is the region of vigorous etching. It is, therefore, seen that the current density measurements explain in a very general manner the formation of variously polished bands and also how the steep fall in current density round about the point M gives rise to a frittered region (III), separated by the two well-polished regions.

On the other hand, the study of potential distribution (*see* Fig. 4) over the anode surface does not seem to throw any light on the occurrence of variously polished bands and it is found to vary uniformly from one end of the plate to the other, the potential at the high current density end being the highest. Thus, this case highlights the importance of current distribution measurements.

(8) *Simultaneous measurement of current and potential at three definite points over the anode surface for varying total cell currents*

During this investigation, three pairs of electrodes were used, each pair consisting of one Luggin capillary attached to a normal calomel electrode and one current-probe electrode.[3] These three pairs were so arranged that one of them was over the unpolished region at a distance of about 2 cm. from the low current density end of the plate, the second pair over the middle of the plate (at a distance of about 5·5 cm. from the low current density end) and the third pair over the high current density region, *i.e.*, at a distance of about 1·5 cm. from the high current density end of the plate.

The total cell current was increased stepwise (each step being 1 amp.) from 0 to 6 A and at each step the corresponding anode potentials and currents, as indicated by the six probe electrodes, were all recorded within 20–30 seconds. This procedure was repeated at each step while the cell current was decreased from 6A to zero. The values thus obtained are plotted in Fig. 5 as rising and falling curves. The curves (V_1–I_1) are due to the electrode-pair over the high current density region, the curves (V_2–I_2) due to the pair over the middle of the plate and the curves (V_3–I_3) due to the pair over the unpolished region.

On comparing the different curves in Fig. 5 it is seen that the curves V_3–I_3 are more or less straight, showing only one potential at each current value and V increases with current density. On the other hand, the curves V_1–I_1 and V_2–I_2 show well-defined regions of depression, indicating that over the middle and the high current density region of the plate, for two or more different voltages the same current density can prevail thus producing polishing effect at the same place at two different voltages. For instance,

referring to curve V_1–I_1 (rising), it is seen that current readings of above 90 divisions galvanometer deflection (4×10^{-9} A/division) prevail at two widely different voltage ranges, *i.e.*, about 0·5 and 1·2 volts. It is, therefore, possible that near about these two voltages and current regions polishing may occur whereas at an intermediate voltage of 0·85 volts corresponding to the region of lower c.d. there may not be any polishing effect.

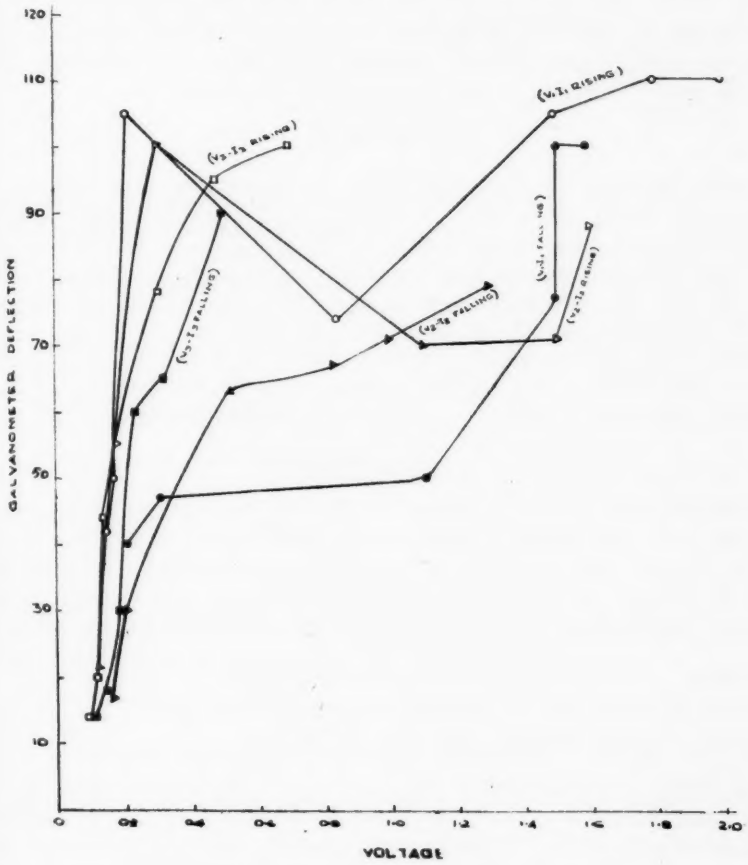

FIG. 5

Those observations and inferences are further corroborated by the I–V curves obtained with one set of moving electrodes which give curves similar in shape to that shown in Fig. 3.

The above studies clearly show that it is the actual current distribution in a Hull cell which determines the observed polishing effects and is responsible for an unpolished region between two polished bands. It may, however, be emphasised that the exact reproducibility of I–V curves is not possible due to other complicating factors rapidly changing with time. However, the results reported above are quite comparable and only some of the typical values, out of several experiments, have been shown here.

Thanks are due to Professor K. S. G. Doss, Director, Central Electrochemical Research Institute, for his helpful suggestions and discussions from time to time.

REFERENCES

1. Sanghi and Ramanathan .. "Electropolishing of copper in orthophosphoric acid bath using a Hull cell," under publication in the symposium special issue of the *Bulletin of the India Section of Electrochem. Soc.*, 1958.
2. ———— .. *Proc. Ind. Acad. Sci.*, 1958, **48 A** (5), 284–87.
3. ———— .. *Curr. Sci.*, 1959, **28**, 23–24.
4. Hull, R. P. .. *Proc. Amer. Electroplaters Soc.*, 27th Convention, 1939.
5. Cuthbertson, J. W. .. *Metal Industry*, August 1951, 87.
6. Skwirzynski, J. K. and Huttly, M. *J. Electrochem. Soc.*, Nov. 1957, **104**, 650.
7. Lorking, K. F. .. *Ibid.*, 1955, **102**, 479.
8. Edwards, J. .. *Ibid.*, 1953, **100**, 198 *c*.
9. Williams, E. C. and Barrett, M. A. *Ibid.*, July 1956, **103** (7).
10. Carl Wagner .. *Ibid.*, 1954, **101**, 225.
11. Sembura, Z. and Michalik, W. *Bulletin de l' Academie Polonaise des Sciences*, 1957, **5** (11), 1073–79.
12. Halfway .. *Electroplating*, 1948, **1**, 205.
13. Walton, H. F. .. *J. Electrochem. Soc.*, 1950, **97**, 219.
14. McG. Tegart, W. J. and Vines, R. G. *Rev. Me't.*, 1951, **48**, 245.
15. Honeycombe, R. W. K. and Hughan, R. R. *J. Council Sci. Industr. Research (Australia)*, 1947, **20**, 297.
16. Jacquet, P. A. .. *Bull. Soc. Chim., France*, 1936, **3**, 705.
17. ———— .. *Trans. Electrochem. Soc.*, 1936, **69**, 629.
18. ———— .. *Metallurgical Reviews*, 1956, **1**, 157.

EMISSION SPECTRUM OF CHLORINE EXCITED IN THE PRESENCE OF ARGON*

Part II. The Band System in the Region 2365-2239Å

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ABSTRACT

The weak band system in the region 2365–2239 Å is discussed in this paper. The wavelengths and the wavenumbers of the bands photographed with the first order of a 21-ft. grating spectrograph are recorded. The vibrational analysis of the bands and their corresponding intensity distribution are also given. The analysis shows that the lower state of the system is the same as that of the 2600–2390 Å system discussed in the earlier paper and is the 3π (O_u^+) state established by Elliott at 17658 cm.$^{-1}$ The constants of the upper state are $\omega_0' = 261{\cdot}5$ cm.$^{-1}$, $\omega_0'x_0' = 0{\cdot}812$ cm.$^{-1}$, $T_0 = 61290$ cm.$^{-1}$

INTRODUCTION

CHLORINE when excited in the presence of argon has been stated in the earlier paper to give two band systems: (1) a strong and extensive system in the region 2600–2390 Å and (2) a weak system in the region 2365–2239 Å. The experimental data and the vibrational analysis of the band system in the region 2600–2390 Å are given in the earlier paper. The present paper deals with the band system in the region 2365–2239 Å.

EXPERIMENTAL DATA AND VIBRATIONAL ANALYSIS

Using the same experimental set-up as described in the earlier paper,[6] the band system was recorded with a Hilger Medium Quartz Spectrograph as well as with a 21-ft. grating spectrograph in the first order. The enlargements of the spectra obtained are shown in Fig. 1. The wavelengths and wavenumbers of the band heads are given in Table I along with their visually estimated relative intensities. The band heads in general appear to be degraded towards shorter wavelengths though there are a number of bands

* Forms a part of the Ph.D. thesis of the author.

for which the degradation is not certain. As the bands are quite weak, the error in the measurements of the positions of band heads may be estimated to be ± 3 cm.$^{-1}$

The vibrational scheme of the band system and the corresponding intensity distribution are given in Tables II and III. The $\triangle G''(v + \frac{1}{2})$ values obtained for this system are in good agreement with those obtained for the 2600–2390 Å system discussed in the earlier paper. All the bands could be fairly well represented by the formula

$$\nu = 43632 + (261{\cdot}5\, v' - 0{\cdot}812\, v'^2) - (255{\cdot}2\, v'' - 5{\cdot}5\, v''^2 - 0{\cdot}0155\, v''^3 + 0{\cdot}00115\, v''^4).$$

The constants used for the lower state of this system are the same as those used for the lower state of the 2600–2390 Å band system which in turn are fairly close to those obtained by Elliott[3] for the 3π (O_u^+) state at 17658 cm.$^{-1}$ from the vibrational analysis of the visible absorption bands of chlorine.

It appears that it would be useful to clarify the confusion that has probably led to the listing of different vibrational constants for the 3π (O_u^+) state in the literature by different people. Elliott[1] in his first paper on the absorption spectrum of chlorine gave the rotational analysis for three bands having origins at 19258 cm.$^{-1}$, 19389 cm.$^{-1}$ and 19509 cm.$^{-1}$ and analysed them as having (v'', v') values as (2, 17), (2, 18) and (2, 19) respectively. He measured also the rotational isotopic shift for the second of these bands and gave 19379·4 cm.$^{-1}$ as the origin of the isotopic band. Birge[2] in his paper presented at the American Physical Society Meeting on December 7th, 1929, stated that to explain isotopic effect it was necessary to decrease Elliott's v' numbering by 2 units. Later Elliott[3] did further experimental work and obtained the rotational constants of four more bands attributed to Cl^{35} Cl^{35} with band origins 17890·9 cm.$^{-1}$, 18076·1 cm.$^{-1}$, 18250·4 cm.$^{-1}$ and 18840·2 cm.$^{-1}$ He analysed also the rotational structure of two weak bands which have origins at 17892·5 cm.$^{-1}$ and 18837·6 cm.$^{-1}$ and which have been attributed to the Cl^{35} Cl^{37} molecule. Elliott states in his second paper that Birge had shown from his (Elliott's) new data that the bands originally designated as (2, 17), (2, 18) and (2, 19) have to be redesignated as (1, 11), (1, 12) and (1, 13). Adopting this change, Elliott assigned the transitions (2, 6), (2, 7), (2, 8) and (2, 12) to the bands having the origins at 17890·9 cm.$^{-1}$, 18076·1 cm.$^{-1}$, 18250·4 cm.$^{-1}$ and 18840·2 cm.$^{-1}$ The weak bands with origins at 17892·5 cm.$^{-1}$ and 18837·6 cm.$^{-1}$ were attributed to the Cl^{35} Cl^{37} molecules with the transitions (2, 6) and (2, 12) respectively. On this

TABLE I

Wavelength, wavenumbers and relative intensities of the bands in the system 2365–2239 *Å*

I	λ_{air}	ν_{vac}	I	λ_{air}	ν_{vac}
0	2364·6	42277	2	2331·2	42883
?	2363·5	42297	2	2330·4	42898
0	2358·9	42380	5	2329·7	42911
1	2358·2	42392	9	2329·2	42920
3	2357·5	42405	8	2328·9	42926
1	2357·1	42412	6	2326·5	42970
1	2356·4	42425	2	2325·7	42985
4	2353·1	42484	2	2325·3	42992
3	2352·5	42495	5	2324·4	43009
1	2352·0	42504	4	2323·3	43029
1	2351·4	42515	4	2322·8	43038
1	2351·0	42522	1	2321·6	43061
4	2350·3	42535	6	2321·1	43070
1	2349·7	42546	2	2320·9	43074
2	2349·1	42558	5	2320·3	43085
4	2346·7	42600	3	2319·4	43101
4	2346·0	42613	4	2317·5	43137
1	2345·1	42629	4	2316·7	43152
0	2344·3	42643	2	2315·9	43167
4	2343·9	42651	4	2315·4	43176
1	2343·7	42655	3	2314·9	43185
2	2343·3	42662	2	2314·1	43200
0	2342·2	42682	0	2312·5	43230
2	2341·3	42698	7	2310·9	43260
7	2340·1	42720	6	2310·3	43271
4	2339·8	42726	5	2309·6	43284
1	2339·4	42733	1	2307·8	43318
?	2338·3	42753	6	2306·8	43337
2	2337·8	42762	2	2306·2	43348
2	2337·3	42771	8	2304·4	43382
5	2336·7	42782	4	2303·7	43395
1	2336·3	42790	4	2303·0	43408
2	2335·1	42812	4	2302·1	43425
1	2334·0	42832	4	2301·4	43438
6	2332·8	42854	10	2298·9	43486

TABLE I (*Contd.*)

I	λ_{air}	ν_{vac}	I	λ_{air}	ν_{vac}
4	2297·4	43514	1	2276·0	43923
4	2296·5	43531	4	2272·6	43989
3	2296·0	43541	3	2271·8	44004
8	2294·6	43567	3	2270·9	44022
1	2293·6	43586	1	2270·1	44037
1	2292·1	43615	0	2269·4	44051
2	2291·2	43632	0	2268·2	44074
?	2290·4	43647	4	2267·6	44086
2	2289·7	43660	0	2266·0	44117
3	2289·1	43672	1	2263·9	44158
0	2288·6	43681	1	2263·1	44174
3	2287·8	43696	0	2261·6	44203
6	2286·7	43718	0	2257·1	44291
6	2285·9	43733	1	2256·2	44309
2	2285·4	43743	0	2253·6	44360
4	2284·2	43765	1	2252·5	44381
2	2283·5	43779	2	2252·2	44387
2	2281·3	43821	2	2251·3	44405
3	2278·6	43873	1	2247·7	44476
2	2278·0	43885	2	2240·0	44629
5	2276·9	43906	2	2238·9	44651

basis he gave the vibrational assignment of all the absorption bands and showed that the assignment was supported by the isotopic shifts observed. Birge's[2] talk at the American Physical Society Meeting was based only on the first published data of Elliott[1] and the correction was apparently meant to be applied for the v' numbering of Elliott in his first paper. With his new data later obtained, Elliott in consultation with Birge decreased each v'' numbering by 1 (not by 2 as originally suggested by Birge) and v' numbering by 6. No further change was necessary in his v'', v' numberings. Weizel,[4] however, applied Birge's original suggestion to Elliott's revised data and decreased the v' numbering by 2 units. The isotopic shifts calculated according to Weizel's analysis are given for comparison in Table IV along with that of Elliott's observed and calculated shifts. It is evident that Weizel's analysis is wrong which is because of the unnecessary correction he applied to the numbering given in Elliott's revised analysis. Herzberg,[5] probably,

TABLE II

TABLE II

Vibrational scheme of the 2365–2239 *Å system of* Cl_2

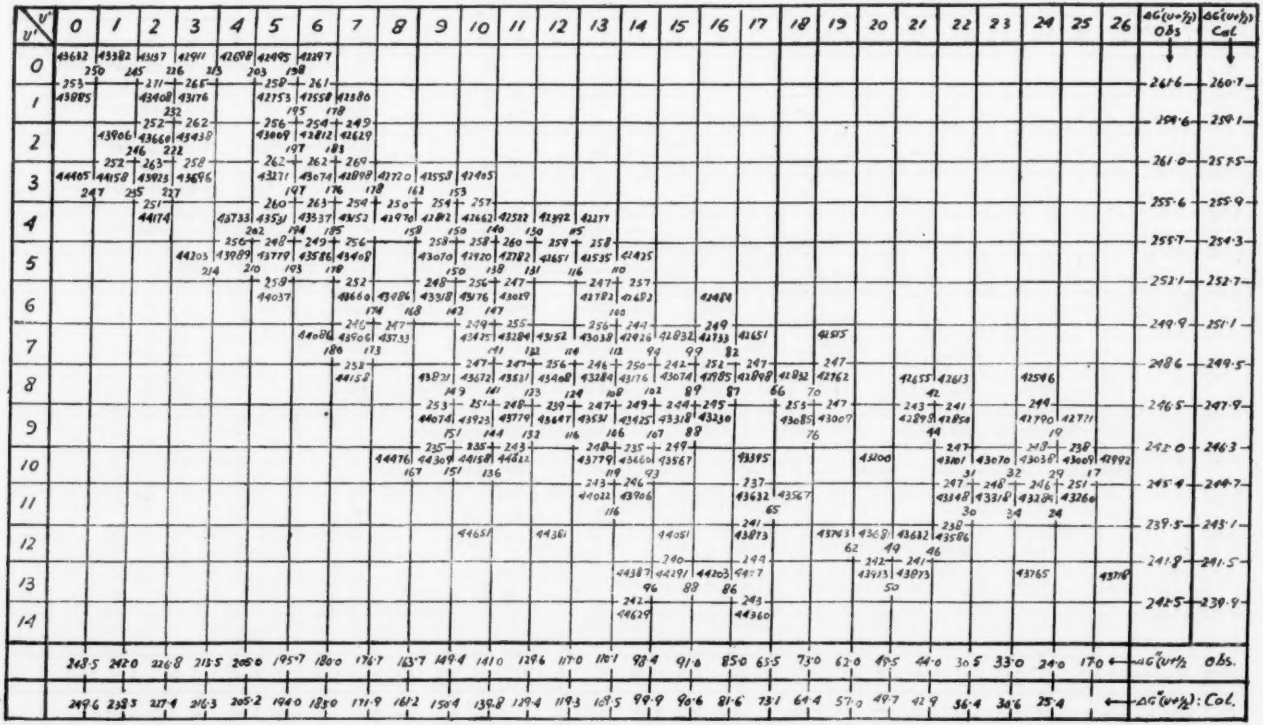
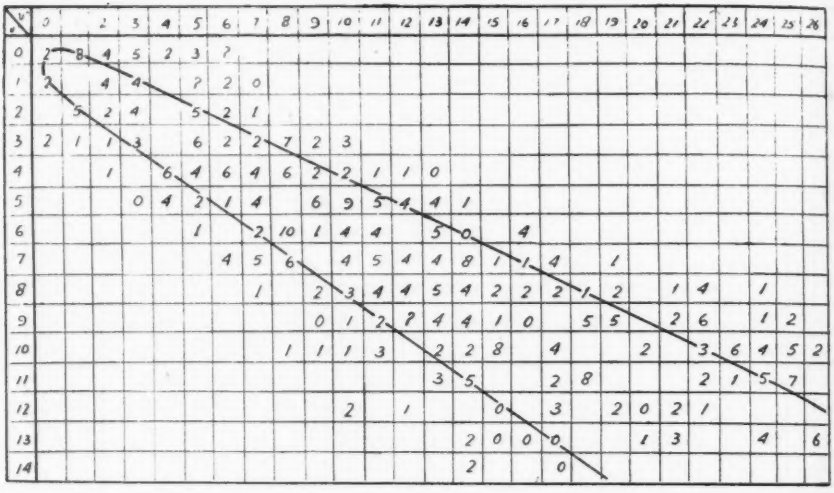


TABLE III

Intensity distribution and Frank-Condon parabola of the 2365–2239 *Å system of* Cl_2



did not take note of this fact while listing the constants given by Weizel in his book.

Assuming that the lower state of the system is 3π (O_u^+) established by Elliott at 17658 cm.$^{-1}$, the position of the upper state comes out to be 61290 cm.$^{-1}$

ISOTOPIC SHIFTS

If one assumes that the vibrational analysis shown in Table II corresponds to $Cl^{35}\,Cl^{37}$ molecule, about 26 bands of that table can be accounted to have isotopic components corresponding to $Cl^{35}\,Cl^{37}$. Table V shows the observed and calculated values for the probable isotopic displacements. All the isotopic components can also be fitted well in the vibrational scheme of the $Cl^{35}\,Cl^{35}$ molecule with different (v', v'') values and are also shown as such in Table II. As in the case of the band system 2600–2390 Å discussed in the earlier chapter, it is again because of such overlapping that the identification of the isotopic band heads cannot be said to be unambiguous.

TABLE IV

$Cl^{35}Cl^{35}$ ν_{vac}	$Cl^{35}Cl^{37}$ ν_{vac}	$\Delta\nu$ observed	Elliott's assignment		$\Delta\nu$ (calculated from Elliott's assignment	Weizel's assignment		$\Delta\nu$ (calculated from Weizel's assignment
			v''	v'		v''	v'	
19389·0	19379·4	+9·6	1	12	+ 10·1	1	10	+5·4
17890·9	17892·5	−1·6	2	6	− 1·6	2	4	−6·8
18840·2	18837·6	+2·6	2	12	+ 2·9	2	10	−0·5

TABLE V

The probable isotopic shifts for the band system 2365–2239 *Å*

v'	v''	ν in cm.$^{-1}$	I	$\Delta\nu$ (obs.) in cm.$^{-1}$	$\Delta\nu$ (cal.) in cm.$^{-1}$
3	10	42405	3	7	8
		42412	1		
0	5	42495	3	9	14
		42504	1		
7	19	42504	1	11	9
		42515	1		
8	22	42600	4	13	16
		42613	4		
2	7	42629	1	14	9
		42643	0		
7	17	42643	1	8	7
		42651	4		
3	8	42720	-7	6	7
		42726	-4		
1	5	42753	?	9	9
		42762	2		
8	17	42883	2	15	10
		42898	2		

TABLE V (*Contd.*)

v'	v''	ν in cm.$^{-1}$	I	$\Delta\nu$ (obs.) in cm.$^{-1}$	$\Delta\nu$ (cal.) in cm.$^{-1}$
9	21	42883	2	15	18
		42898	2		
9	19	42992	2	17	16
		43009	5		
8	15	43061	1	13	9
		43074	2		
9	18	43070	6	15	14
		43085	5		
10	22	43074	2	27	23
		43101	3		
8	14	43167	2	9	8
		43176	4		
1	3	43176	4	9	5
		43185	3		
11	22	43318	1	30	26
		43348	2		
9	13	43514	4	17	11
		43531	4		
11	18	43541	3	26	21
		43567	8		
11	17	43615	1	17	19
		43632	2		
8	10	43660	2	12	8
		43672	3		
11	14	43885	2	21	17
		43906	5		
11	13	44004	3	18	17
		44022	3		
10	9	44291	0	18	15
		44309	1		
3	0	44387	2	18	12
		44405	2		
12	10	44629	2	22	20
		44651	2		

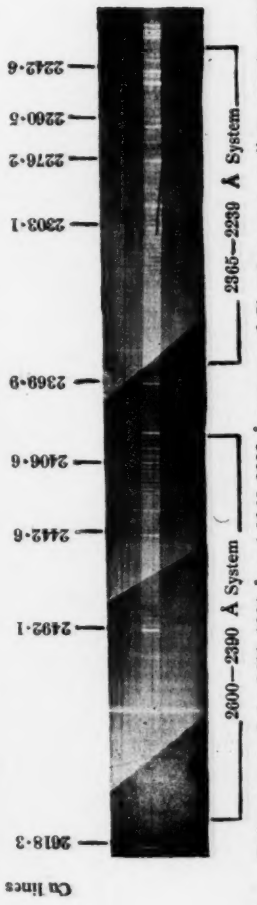


FIG. 1 *a*. Enlargement of the 2600–2390 Å and 2365–2239 Å systems of Cl_2 taken on a medium quartz spectrograph.

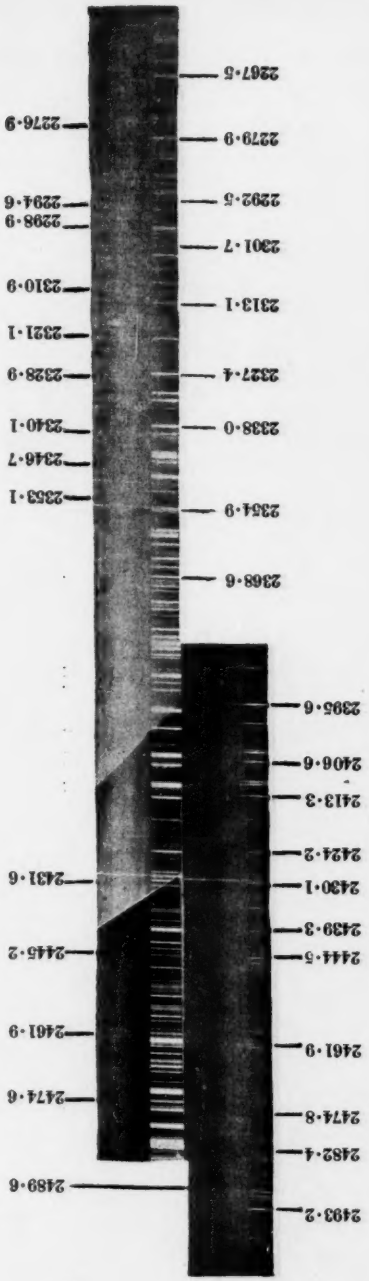


FIG. 1 *b*. Enlargement of the 2365–2239 Å system of Cl_2 taken with a 21-feet grating spectrograph in the first order.

ACKNOWLEDGEMENT

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REFERENCES

1. Elliott, A. .. *Proc. Roy. Soc., London*, 1929, **123**, 629.
2. Birge, R. T. .. *Phys. Rev.*, 1930, **35**, 133.
3. Elliott, A. .. *Proc. Roy. Soc., London*, 1930, **137**, 638–57.
4. Weizel, W. .. *Hand. Buch Der Experimental Physik*, 1931, Band I, 375–78.
5. Herzberg, G. .. *Molecular Spectra and Molecular Structure—Part I. Spectra of Diatomic Molecules*, p. 510.
6. Venkateswarlu, P. and Khanna, B. N. *Proc. Ind. Acad. Sci.*, 1959, **49**, 117.

PHOTO-MESONS FROM POLARIZED NUCLEONS

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1. Introduction

Photo production of pions by nucleons is fairly well understood for energies up to above three or four hundred MEV. The resonance predicted by theory of Chew and Low at about 300 MEV has been experimentally confirmed. However the behaviour of photo production cross-section at higher energies say above 700 MEV is still an open question. The calculations for energies higher than 500 MEV are done on the understanding that only low energy intermediate states are important for low energy processes and hence are not successful in explaining the important features of the phenomena. In such calculations, an improved solution of the Chew-Low amplitude is sought by including the corrections from two and possibly three meson states and these corrections are much smaller than what has been actually observed. Thus it would be worthwhile investigating other features of Chew-Low cross-section at low energy and their agreement with photo production experiments. One such feature relates to the polarisation phenomena. In this note, we shall examine the angular distribution of mesons produced by polarised photons taking into account the spin states of the nucleon.

2. Angular Distribution of Neutral Mesons Resulting from a Polarized Photon Beam

We shall first consider the production of neutral mesons and the charged ones will be dealt with in the next section. The amplitude for π° photo production by a nucleon is given by (Chew and Low, 1956)

$$F(\pi^\circ) = \frac{ef}{\sqrt{2\omega k}} \left(\frac{\mu_p + \mu_n}{2M}\right) \frac{i\vec{\sigma} \cdot \left[\vec{q} \times \left(\vec{k} \times \vec{\epsilon}\right)\right]}{\omega}$$

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§ Government of India Senior Research Scholar.

$$-\frac{e}{f}\left(\frac{\mu_p-\mu_n}{4M}\right)\frac{1}{2\sqrt{\omega k}}\left[\vec{q}\cdot\left(\vec{k}\times\vec{\epsilon}\right)\left(\frac{a_1+4a_2+4a_3}{3q^2}\right)\right.$$

$$\left.+i\vec{\sigma}\cdot\left\{\vec{q}\times\left(\vec{k}\times\vec{\epsilon}\right)\right\}\left(\frac{a_1+a_2-2a_3}{3q^2}\right)\right] \qquad (1)^*$$

where μ_p, μ_n are the magnetic moments of the proton and the neutron respectively. $\vec{k}$ is the momentum of the photon, $\vec{\epsilon}$ its direction of polarization while $\vec{q}$ is the pion momentum. a's are the pion nucleon scattering amplitudes. The term proportional to $(\mu_p+\mu_n)$ can be neglected in comparison with the second term though its inclusion does not in any way affect the results of the paper.

Let us choose a co-ordinate system with z-axis in the direction of the photon propagation. (1) gives the following amplitudes for right and left circularly polarized photons:

$$F_{r.c.}(\pi^\circ)=-\frac{ie}{f}\left(\frac{\mu_p-\mu_n}{8Mq}\right)\sqrt{\frac{k}{\omega}}\left[-\frac{a_1+4a_2+4a_3}{3\sqrt{2}}e^{i\phi}\sin\theta\right.$$

$$\left.+\frac{a_1+a_2-2a_3}{3}\left(\frac{\sigma_s}{\sqrt{2}}e^{i\phi}\sin\theta-\sigma_+\cos\theta\right)\right] \qquad (2)$$

$$F_{l.c.}(\pi^\circ)=-\frac{ie}{f}\left(\frac{\mu_p-\mu_n}{8Mq}\right)\sqrt{\frac{k}{\omega}}\left[\frac{a_1+4a_2+4a_3}{3\sqrt{2}}e^{-i\phi}\sin\theta\right.$$

$$\left.+\frac{a_1+a_2-2a_3}{3}\left(\frac{\sigma_z}{\sqrt{2}}e^{-i\phi}\sin\theta-\sigma_-\cos\theta\right)\right] \qquad (3)$$

θ is the angle between the vectors $\vec{k}$ and $\vec{q}$ while ϕ is the angle which the projection of $\vec{q}$ makes with the x-axis. $F_{r.c.}$ and $F_{l.c.}$ matrices in the spin space of the nucleon. Since (2) and (3) are derived in the assumption that the nucleon has no motion, it has a definite spin orientation. Let us assume that the direction coincides with that of photon propagation. It follows from (2) that spin flip cross-section is zero for a right circularly polarized photon beam and that the non-spin flip cross-section is given by

$$\frac{d\sigma_{r.c.}(\pi^\circ)}{d\Omega}=\frac{e^2(\mu_p-\mu_n)^2}{(16\pi Mqf)^2}\left(\frac{kq}{2}\right)|a_2+2a_3|^2\sin^2\theta \qquad (4)$$

* Throughout this paper we use natural units, *i.e.*, $\hbar=c=1$. The energy of the charged pion (139·6 MEV) will serve as the energy unit and its compton wavelength as the unit of length. In these units M the rest of the nucleon is 6·72.

On the other hand, a left circularly polarized beam yields both spin flip and non-spin flip cross-sections:

$$\frac{d\sigma_{l.c.}^{(1)}(\pi^\circ)}{d\Omega} = \frac{e^2(\mu_p-\mu_n)^2}{(16\pi\,\mathrm{M}fq)^2}\binom{kq}{18}\,|\,2a_1+5a_2+2a_3\,|^2\sin^2\theta \tag{5}$$

$$\frac{d\sigma_{l.c.}^{(2)}(\pi^\circ)}{d\Omega} = \frac{e^2(\mu_p-\mu_n)^2}{(16\pi\,\mathrm{M}qf)^2}\binom{kq}{9}\,|\,a_1+a_2+2a_3\,|^2\cos^2\theta \tag{6}$$

We have used superscripts (1) and (2) to denote non-spin flip and spin flip cross-sections.

We note that if we have the nucleon polarized opposite to the direction of propagation of photon, it is the right circular photon that will yield non-zero spin flip amplitude while the spin flip amplitude arising from a left circular photon is zero. The above results also bring out the need for polarizing the target nucleon.

3. CHARGED PIONS

The complete amplitude for photo production of a positively charged meson is given by

$$\begin{aligned}\mathrm{F}(\pi^+) = \frac{ef}{\omega}\Bigg[&\vec{i\sigma}\cdot\vec{\epsilon}+2i\frac{\vec{\sigma}\cdot\left(\vec{k}-\vec{q}\right)\left(\vec{\epsilon}\cdot\vec{q}\right)}{1+\left(\vec{k}-\vec{q}\right)^2}\\&+\frac{\mu_p-\mu_n}{4\mathrm{M}f^2}\left\{\left(\vec{q}\cdot(\vec{k}\times\vec{\epsilon})\right)\left(\frac{a_1+a_2-2a_3}{3q^2}\right)\right.\\&\left.+i\sigma\cdot\left(\vec{q}\times(\vec{k}\times\vec{\epsilon})\right)\left(\frac{a_1-2a_2+a_3}{3q^2}\right)\right\}\\&-\left(\frac{\mu_p+\mu_n}{2\mathrm{M}}\right)\frac{\vec{i\sigma}\cdot\left(\vec{q}\times(\vec{k}\times\vec{\epsilon})\right)}{\omega}\Bigg]\end{aligned} \tag{7}$$

where the first two terms in the bracket are respectively the s-wave "guage" contribution and the "pion current" contribution. We can proceed in exactly the same way as in the previous section and calculate the amplitudes for a positively charged pion production by left and right circular photons. However, we note that due to the presence of the pion current term, spin flip and non-spin-flip amplitudes occur for both the cases. The pion current term is important only for small angles and we can neglect it since it is proportional to $\sin^2\theta$. Thus we find that even in the case of charged pions the

cross-sections for right and left circular photons are of the same form as for neutral mesons. We give below for completeness the various cross-sections for the production of a positive pion:

$$\frac{d\sigma_{r.c.}(\pi^+)}{d\Omega} = \left(\frac{\mu_p - \mu_n}{8\pi M f}\right)^2 \frac{e^2}{4}\frac{k}{q} \mid a_3 - a_2 \mid^2 \sin^2\theta \tag{8}$$

$$\frac{d\sigma_{l.c.}^{(1)}(\pi^+)}{d\Omega} = \left(\frac{\mu_p - \mu_n}{8M\pi f}\right)^2 \frac{e^2}{36}\frac{k}{q} \mid 2a_1 - a_2 - a_3 \mid^2 \sin^2\theta \tag{9}$$

$$\frac{d\sigma_{l.c.}^{(2)}(\pi^+)}{d\Omega} = \frac{qe^2f^2}{4\pi^2}\left| 1 - \frac{(\mu_p - \mu_n)k}{12Mf^2q}(a_1 + a_3 - 2a_2)\cos\theta \right|^2 \tag{10}$$

We note from equations (4), (5) and (6) that the cross-section for a right circular photon is proportional to $\sin^2\theta$ while that for a left circular photon is proportional to $\cos^2\theta$. In the case of positive pion production, the difference in angular distribution is more pronounced. The positive pions arising from left circular photons is distributed according to the law $A + B\cos\theta + C\cos^2\theta$. These features can be checked against experiments by using a polarized beam on a polarized nucleon target.

In conclusion, we wish to thank Mr. R. Vasudevan for interesting discussions.

Summary

It is shown that the angular distribution of photo-mesons obtained from polarized nucleons behaves differently for left and right circularly polarized beams.

Reference

1. Chew, G. F. and Low, F. E. .. *Phys. Rev.*, 1956, **101**, 1579.

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